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INSTRUMENTATION FOR MONITORING SPECIFIC PARTICULATE SUBSTANCES IN STATIONARY SOURCE EMISSIONS

MONSANTO RESEARCH CORPORATION

PREPARED FOR

ENVIRONMENTAL PROTECTION AGENCY

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This report describes the development of an engineering prototype analytical and sampling system capable of monitoring continuously the concentration of beryllium and cadmium in typical stationary source emissions. Data for laboratory tests with radio-frequency and AC arc induced emission spectroscopic systems are reported. Information derived from field testing of the AC arc induced emission spectroscopic system at a power plant is described. Briefing documents describing technology appropriate to the problem of continuous measurement of beryllium, cadmium, mercury, lead, arsenic, antimony, barium, boron, chromium, copper, manganese, nickel, and vanadium from stationary emission sources are also presented in the appendices.

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Barium
Boron
Chromium
Copper
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Nickel
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ABSTRACT

The results of a research program addressed to instrumentation or methods for monitoring specific metals in stationary source emissions is reported. The program had two distinct objectives:

(a) To produce an engineering prototype analytical and sampling system capable of continuously monitoring the concentration of beryllium and cadmium in typical stationary source emissions; and

(b) To prepare briefing documents which identify technology appropriate to the analytical problem of continuous measurement of beryllium, cadmium, arsenic, antimony, barium, boron, chromium, copper, lead, manganese, mercury, nickel, and vanadium in stationary source emissions.

Based upon the briefing document on analytical techniques for beryllium and cadmium (Appendix II), two candidate continuous monitoring techniques were chosen for application studies; radio-frequency induced emission spectroscopy and AC arc-induced emission spectroscopy. A feasibility study of the radio-frequency induced plasma system indicated that the system could not be applied to continuously flowing sample gases containing air, even though a detection limit of 0.4 μg Cd/m^3 was obtained in an argon matrix.

The AC arc-induced emission spectroscopy studies were conducted employing an engineering prototype based on the Webb-arc cell. This system is potentially useful for continuous monitoring of any metal by employing a monochrometer to select specific atomic emission lines of the various metals. Laboratory testing of this system indicated detection sensitivities for beryllium at the 1 μg/m^3 level. The corresponding sensitivity for cadmium was very poor and time did not permit optimization of the continuous monitor for cadmium detection. Considerable difficulty was encountered in limited field tests of the Webb-arc system at a coal-fired power plant when the prototype continuous monitoring system was interfaced with the flue gas effluent. In spite of these difficulties, the Webb-arc emission spectroscopic system is considered the most promising approach to monitoring trace metals in work environments and stationary source effluents. Advantages of the arc-induced emission spectroscopy approach are: (a) direct, real-time, continuous measurements down to low trace levels 1 μg Be/m^3 without emission signal integration; (b) high specificity, (c) moderate volume flow rates (up to 40 l/min); and (d) relatively simple, low-weight instrument package. The applicability of the Webb-arc induced emission spectroscopy techniques to direct continuous monitoring of Be, Cd, and other potentially toxic metals requires further study.

FOREWORD

Airborne particulate matter is a major air pollutant having significant effects on health, economics, ecology, visibility, and aesthetics. Effective techniques and hardware systems for source emissions measurement are needed for application to the various sources to achieve control of particulate emissions and thus protect the environment.

Available information reveals the major sources of air pollutants containing toxic metallic species emanate from: the combustion of fuels containing such metals either as impurities or as fuel additives; metal refining and metallurgical operations; operations involving metals fabrication or machining; and waste disposal. Many such compounds have been found in our waters and our air. Historical records of analysis of surface water and atmospheric samples indicate a trend of increasing amounts of these contaminants. The development of improved control technology, control practices, and emission information requires instrumentation or methods to measure and monitor these particular substances.

This contract work was sponsored by the National Environmental Research Center at Research Triangle Park, North Carolina, to identify promising techniques applicable to monitoring the concentration of the specific trace metal components in typical stationary source emissions and to produce and test an engineering prototype, based on existing technology through adaptation of existing analytical instrumentation, for measurement of beryllium and cadmium.

This report is included in the Environmental Protection Technology series - the series, devoted to new or improved technology required for control and treatment of pollution sources to meet environmental quality goals, includes reports of work dealing with research, development, and demonstration of instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution.

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John O. Burckle
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1. DISCUSSION OF REPORT FORMAT

This report contains information on two interrelated, but separate, general tasks. Task I was to produce an engineering prototype analytical and sampling system capable of monitoring continuously the concentration of beryllium and cadmium in typical stationary source emissions. The task includes identification and development of a workable detection concept, evaluation of the sampling problem, fabrication of a prototype analytical and sampling system, and laboratory and field testing of the analytical and sampling system.

Task II involved the preparation of detailed briefing documents based on a thorough review of the literature, which identify technology appropriate to the analytical problem of continuous measurement of beryllium, cadmium, mercury, lead, arsenic, antimony, barium, boron, chromium, copper, manganese, nickel, and vanadium from stationary emission sources.

To cope with the mass of data accumulated in both tasks, a special report format was adopted. A summary of all data and the conclusions and recommendations derived from laboratory and field testing of the prototype monitors and from the literature surveys are presented in the Executive Summary (Section 2).

Task I data are reported in Sections 3, 4, 5, and 6, which cover (a) Summary of Literature Survey and Briefing Documents, (b) Preliminary Field Studies, (c) Instrument Design and Laboratory Testing, and (d) Field Testing of Prototype, and in Appendices I and VII, which describe in detail (a) Sampling System considerations and Design and (b) Operational and Maintenance Manual - RF and Arc Excited Emission Spectroscopic Systems. Task II data are reported in Section 3 (Summary of Literature Survey and Briefing Documents) and Appendices II to VI, which are detailed briefing documents on analytical techniques for continuous monitoring of (a) Be and Cd, (b) Hg, (c) Pb, (d) As and Sb, and (e) Ba, B, Cr, Cu, Mn, Ni and V, in stationary emission sources.

1.1 Format of Appendices

Seven appendices describe (a) detailed discussion of sampling problems; (b) five detailed briefing documents for (1) Be and Cd, (2) Hg, (3) Pb, (4) As and Sb, and (5) Ba, B, Cr, Cu, Mn, Ni and V; and (c) operating manual and maintenance manual for Be/Cd monitoring system.

1.1.1 Briefing Document Format

The briefing documents were prepared to show potential methods of analysis, some of the limitations of the techniques, possible problems in applying the procedures, and recommendations for the most acceptable approaches. Emphasis was placed on five prime factors, analytical reliability (accuracy and precision), selectivity, sensitivity, a continuous operation mode, and speed. Other factors (personnel, apparatus, installation, and maintenance requirements and costs) although important, can be controlled by proper hardware design and are emphasized to a lesser degree.

Since some of the chemical and physical properties of the elements and their compounds will markedly influence the selection of the analytical technique, a brief commentary on selected properties for emissions anticipated from known sources is included in a preface for each element. Potential analytical approaches, based on the chemical or physical properties are then presented.

Wherever specific analytical approaches have been used to monitor an element, a detailed outline of the principle, applicability, and operational parameters is tabulated. These detailed outlines generally highlight the merits and limitations of potential methods.

In several cases, candidate analytical methods have not been applied to the element of interest. As a consequence, specific information regarding operational parameters and response factors are not available. In the briefing document, the technique is described by indicating the principles involved, potential applicability, and anticipated problems.

Many manual techniques currently used for monitoring trace metal emissions, while meeting criteria of analytical reliability, selectivity, and sensitivity, require moderate to lengthy time periods for sample pretreatment and are not considered or evaluated in this document. An analytical method was not eliminated simply based on need for preliminary pretreatment, but was screened based on whether the treatment, including chemical reactions, could be performed at the site, unattended, and within a total measuring time of five to ten minutes.

Each briefing document is assembled as a separate entity containing its individual table of contents and sets of references.

1.1.2 Format of Operating and Maintenance Manuals

The operating and maintenance manuals are comprised of manuals supplied by the manufacturers of individual sub-systems and procedures developed under the experimental laboratory and field testing phases of this program.

2. EXECUTIVE SUMMARY

2.1 Program Objectives

The principal program objectives were:

(a) To produce an engineering prototype analytical and sampling system capable of monitoring the concentration of the specific trace metal components - beryllium and cadmium - in typical stationary source emissions.

(b) To prepare briefing documents which identify technology appropriate to the analytical problem of continuous measurement of beryllium, cadmium, mercury, lead, arsenic, antimony, barium, boron, chromium, copper, manganese, nickel and vanadium.

2.2 Program Approach

The program consisted of the following tasks:

1. Literature survey to identify the technology required to select an analytical approach and to determine potential problems in applying the monitor to typical Be and Cd stationary emission sources - power plant, incinerator, and refinery or machining operation.
2. Preparation of briefing documents describing analytical technology related to continuous measurement of Hg, Pb, As, Sb, Ba, B, Cr, Cu, Mn, Ni, and V.
3. Preliminary field studies to determine (a) the level of the Be and Cd emission from the power plant, incinerator, and refinery or machining operation; (b) physical and chemical nature of the emissions; and (c) potential problems in interfacing the monitor and sampling system with the stack.
4. Selection of analytical approach based on literature survey and evaluation of preliminary field studies.
5. Design and fabrication of monitor and sampling system.
6. Laboratory feasibility testing and calibration of the monitor and sampling systems to establish response characteristics, interferences, and sampling problems.
7. Field testing of the prototype monitor and sampling system.

The selection of a system for "continuous monitoring" depends on several factors: the nature of the source, the sampling constraints, and the availability of an analytical technique compatible with these. The selection of an analytical approach is further influenced by the definition of continuous monitoring and by the necessary requirement for a pretreatment step. Continuous monitoring can be defined in a very restrictive sense as being only real-time measurement with no sample pretreatment. However, the present technology in abatement control and detection systems permits only an approximation of continuous sampling and measuring. Methods considered during the selection phase of the program included semi-automatic techniques which required sample concentration or pretreatment of the specimen including chemical reactions that could be performed at the site, unattended, and within a total measuring time of five to ten minutes.

The following evaluation parameters were used to select the analytical technique for the Be/Cd monitor: Specificitv, sensitivity, range, accuracy, precision (repeatability), operational mode, sampling time, analysis time, total cycle time, calibration technique, sample form, interferences, unit output, special equipment required, multi-element application, safety hazards, problem areas, routine maintenance, volume flow rate, estimated instrument cost, estimated size and weight, and compatibility with beryllium (or cadmium).

The selection of the proper analytical technique depends not only on the response factors of the detection system, but also on the physical and chemical properties of the total emissions. Consideration must be given to:

Rate of emission of Be and Cd, weight/volume of effluent, and total volume rate of exhaust.

Overall composition of emission, including potential interferences (gases, aerosols, and other metals).

Temperature/pressure conditions at source emission point.

Representative particle size distribution of particulate emitted.

Distribution of Be and Cd within this size distribution.

The process data suggests the sensitivity and resolution requirements of the monitor, its concentration span, the potential sources of interference (chemical and physical) that it must cope with, and the requirements of sampling and delivery equipment to ensure that a representative sample is presented to the analyzer.

In evaluating the candidate analytical technique for either real-time continuous or intermittent monitoring, the following questions related to the properties of the source emission must be answered:

1. Is the technique sufficiently sensitive to detect Be and Cd at the level of emission on an instantaneous or integrated sample basis? Does a large variation in concentration adversely influence the quantitative reponse of the detection system?

2. Is the effluent velocity too fast for quantitative instrument response for real-time analysis? Is the velocity too fast for a filter, impinger or electrostatic collection system?

3. Are the elements being measured present as particulate, mist or vapor? Will the analytical technique measure total amount of element in solid, liquid or gas phases?

4. Will other components of the effluent (gases, aerosols and metals) interfere with the analytical measurements?

5. Will the temperature/pressure conditions at the source emission point affect the operation of the analytical system? Will variations in these parameters affect the precision of the measurement?

6. What effect does particle size distribution have on the accuracy and precision of the measurement? If sample is measured in real-time, are large and small particles measured equally? If a sample must be isolated from the vapor stream, will a representative specimen be obtained? (Note - Filtration presents special problems. While filters are capable of retaining particles of all sizes, the filtration efficiency varies with particle size and inertial parameter between about .5 and .05 µm. Use of such filters also introduces additional matrix problems.) Can particulate, fume and vapor containing Be and/or Cd be trapped quantitatively with filters, impingers or by chemical reactions?

7. How randomly are Be and Cd distributed within the particulate? What influence does this distribution have on the precision of the analytical measurement?

The chemical and physical properties of beryllium and cadmium and their compounds differ considerably between each element and, as expected, profoundly influence the selection of methods for quantitative analysis. Analytical techniques that can be applied to one element and its compounds cannot necessarily be applied to the other.

Fundamental differences in atomic structure and nature of compound formation for each element restrict application of certain analytical techniques based on nuclear or atomic properties to individual elements and their compounds and do not allow application for analyses of both elements by the same technique. Analytical techniques for trace analyses based on x-ray emission of characteristic radiation for cadmium (atomic number 48) cannot be applied to beryllium (atomic number 4). Conversely, photoneutron excitation techniques which can be applied to beryllium cannot be used with cadmium.

Spectrographic methods have been devised for trace analyses of both elements, beryllium and cadmium. However, differences in volatility and attendant response factors influence operating conditions for attaining maximum sensitivities for each element. Beryllium and its oxides (low fired and high fired) are less volatile and more refractory than cadmium and cadmium oxide.

In selecting a continuous monitoring device for both beryllium and cadmium emissions from stationary sources, there are two options. Two analytical methods, based on measuring different properties and requiring different measuring systems and optimized for maximum response can be incorporated into one monitor. However, the more ideal alternative would be to select one measuring system which is highly selective and responsive to both elements.

At the present state-of-the art, there is no analytical technique available for universal application as a direct, continuous, monitor of beryllium and cadmium from all types of stationary source emissions at the A.C.G.I.H. 1967-TLV levels of 0.002 mg Be/m^3 and 0.02 mg Cd/m^3 (as soluble salts and metal dust) or 0.1 mg Cd/m^3 (as CdO fume).

A variety of analytical techniques, including colorimetry, fluorimetry, emission spectroscopy, atomic absorption spectrophotometry, gas chromatography, and electrometric measurements have been used routinely in monitoring beryllium effluents and atmospheric pollution. Somewhat similar approaches, i.e., colorimetry, emission spectroscopy, and atomic absorption spectrophotometry, plus polarography have been applied for measuring cadmium in dusts and fumes. These procedures employ standard analytical instrumentation and require collection in an impinger, electrostatic precipitator, or on a filter followed by low-temperature ashing or acid digestion prior to the actual analytical measurement. The techniques have proven useful for first generation monitoring but require moderate to lengthy time periods for sample pretreatment, are prone to contamination from reagents and the digestion processes, and are not usable for on-site, continuous monitoring of source emissions.

The prime candidates for a continuous monitor of metal emissions from stationary sources are based on radiant energy emission or absorption, and measurement of nuclear properties and radioactivity. The techniques potentially suitable for sensors for automated, continuous analysis are:

Emission spectroscopy
Flame photometry
Atomic absorption or fluorescence spectroscopy
X-ray emission (fluorescence)
Activation analysis
Mass spectrography

Conventional x-ray emission (fluorescence) techniques can be applied to Cd, but not to Be. Continuous monitoring devices and manual analytical procedures based on activation analysis have been used to determine Be, but are not applicable to Cd. A number of problems with low ionization efficiencies and multi-ion fragments occur when applying mass spectrography to measuring Be and Cd. Triply ionized aluminum ($^{27}Al^{3+}$) and doubly ionized oxygen ($^{18}O^{2+}$) can interfere with the ion, $^{9}Be^{+}$. The spectoscopic techniques - emission, flame photometry, and atomic absorption or fluorescence - also require somewhat different operating conditions to obtain maximum response for either Be or Cd. With the spectroscopic techniques, the problem is more serious with the flame techniques - flame photometry and atomic absorption or fluorescence - than with continuous, flow-through, emission spectroscopy.

Several continuous, flow-through, monitoring systems based on the spectrographic measurement of arc (or spark) induced optical emission characteristics of beryllium have been developed and used successfully for measuring the beryllium levels (down to $<1\ \mu g/m^3$ of air) in beryllium production or manufacturing operations (See Appendix II, Sections 4.1.1 to 4.1.2). The sensitivity (detection limit $\leq 1\ \mu g\ Be/m^3$ of air), speed (instantaneous, or if integration is used approximately 20-30 seconds), and selectivity (specificity - good, but dependent on the monochromator and nature of the sample) demonstrated by the Webb system (ref. 1,2), made the flow-through emission spectroscopic techniques very attractive for satisfying the needs of this program for continuous, real-time (or 20-30 second response times), monitoring for trace metal analyses. The technique has been used in several atomic energy projects for monitoring beryllium levels in work environments and in production facilities (ref. 1,2).

The analytical approaches used in the current study are based on the flow-through emission spectroscopic techniques (ref. 1,2). The program was developed with emphasis on current monitoring needs, as a function of the state-of-the-art. Continuous monitoring was interpreted as having combined sampling and analysis times of less than 5 minutes, or more appropriate as instantaneous or a maximum of 20-30 seconds.

When emphasizing current monitoring needs, we found that the problems related to sampling and monitoring Be and Cd in emissions of widely different physical and chemical composition require better definition. To better understand the sampling and monitoring requirements, preliminary sampling studies were performed at a power plant, incinerator, and a beryllium machining operation. Obviously, the problems are less acute in monitoring beryllium or cadmium in operations where either element or its compound, although existing at a low concentration in the stack gas, constitutes the major portion of the particulate or fume. The most complex sampling and analytical problems would be encountered in the power plant or incinerator emissions where the concentration of Be and Cd are low in a particulate matrix containing relatively high amounts of other elements in refractory compounds.

Although Webb, et al. (ref. 1,2) demonstrated that the flow-through emission spectroscopic technique could be applied successfully to monitoring low levels (<1 μg Be/m^3 to 100 μg Be/m^3), the data also suggested that larger amounts of energy would be necessary to vaporize relatively large (>>1 mg/m^3) quantities of refractory materials encountered in power plant emission sources and to excite Be in these effluents to produce optical emission spectra. As a consequence, emphasis was placed on developing a higher source of excitation energy with a radiofrequency (RF) plasma. However, in addition, an arc cell was borrowed from Webb to establish feasibility for application to detecting Be emissions in power plant effluents.

2.3 Findings

2.3.1 Preliminary Field Tests for Problem Identification (See Section 4 and Appendix I)

Samples of particulate were obtained with a cascade impactor from stack emissions from three test sites - coal fired power plant, solid waste municipal incinerator, and a beryllium alloy machining operation. Sampling was accomplished with the flow rate through the nozzle of the set below isokinetic velocity to favor collection of larger particles. The non-isokinetic condition was established to determine if a reasonably representative dust sample could be obtained without isokinetic sampling.

The measurements showed that more than 80% of the particulate collected from the power plant had diameters below 5 microns. These data suggest that a reasonably representative particulate sample could be obtained below isokinetic conditions.

Atomic absorption spectrophotometric analyses of particulate on individual stages of the cascade impactor indicate concentrations in the flue gas of the power plant of approximately 30 μg Be/m^3 and 1.2 μg Cd/m^3 in particles with diameters between 0.24

micron and 7.0 microns. The limited data suggest that the beryllium content is lower in the smaller particles than in the larger particles, whereas the opposite relative distribution appears to hold for cadmium.

Difficulties in sampling the municipal incinerator were encountered due to high moisture content of the stack effluent. Unless proper temperature control was maintained, most of the material collected as a water condensate in the cyclone prior to the separation stages. When condensation occurred, no beryllium was detected in the impactor stages which would isolate particulate in the 0.24 micron to 7.0 micron range; however, very small quantities of cadmium were detected in a relatively uniform distribution in 4 of the 5 stages in the same particle size range. When condensation was minimized, concentrations of approximately 0.4 to 2 μg Be/m³ and 40 μg Cd/m³ were collected in the particle size range of 0.24 micron to 7.0 microns; the distribution of beryllium appears to be approximately the same in the 4 stages through the particle size range of 0.36 micron to 7.0 microns, but slightly lower in the range 0.24-0.36 micron. The distribution of cadmium in the various stages of the cascade impactor is markedly different from that observed for beryllium; quantities of cadmium are greater on the stages that isolate the smaller particles 0.24 micron to 1.1 microns, than on the stages 1.1 microns to 7.0 microns.

No particulate was isolated when sampling the beryllium machining operation, with filtering devices which could retain >0.2 micron particles. In this preliminary study, no attempt was made to provide means for sampling vapor or "fume" in impinger solutions or other media.

2.3.2 Laboratory Tests on Emission Spectroscopy With Radio-Frequency Induced Plasma and Webb-arc Cell (See Sections 5.2 and 5.3 and Appendix VII)

A feasibility study was conducted to determine if a radio-frequency (RF) induced plasma system could be applied as a high energy source for a continuous monitor based on emission spectrographic measurements for Be and Cd. Although a detection limit of 0.4 μg Cd/m³ of argon was obtained in pure argon by direct measurement, without signal integration, the system could not be applied with continuously flowing sample gases containing air.

This study showed that although radio-frequency induced plasma temperatures as high as 20,000°K can be attained at atmospheric pressure, the detection of the emission spectra of trace metals is extremely difficult when using air or air-enriched argon as the matrix gas. The plasma temperatures are sufficiently high to vaporize most refractory compounds and the excitation energies (up to 25 electron volts) provide the necessary electronic excitation to produce excellent emission spectra with argon as the matrix. But with air in the plasma matrix, the plasma shape becomes distorted, increased background emission spectra are obtained, and the line intensities of the element being determined are diminished. As a result direct analytical determinations of cadmium in air matrices were not possible even at levels in excess of 1000 $\mu g/m^3$.

No direct correlation with molecular emission bands, e.g., metal oxide, was obtained under the test conditions. No attempt was made to pursue the potential use of molecular emission bands in this study.

When using the Webb-cell as the excitation source, a detection level was reported by Webb et al. (ref. 1,2) as 1 $\mu g\ Be/m^3$ and was substantiated in a modified (AC arc, rather than pulsed DC arc) cell on this program. No data were reported by Webb et al. (ref. 1,2) for cadmium, but Webb indicated in a private communication that cadmium measurements should not be a problem. However, limited laboratory studies with cadmium aerosols and with the AC arc modification in this program show much poorer sensitivities, which were insufficient to provide detection limits equivalent to the TLV levels [0.02 mg Cd/m^3 (as soluble salts and metal dust) and 0.1 mg Cd/m^3 (as CdO fume)]. Unfortunately, no detailed study was made and data was accumulated only with the instrument conditions used for detecting beryllium. Optimization of conditions for detecting cadmium may provide the needed sensitivity. Undoubtedly, instrument conditions must be optimized for each element.

2.3.3 Field Test of Webb-cell System at Coal-fired Power Plant (See Section 6.0)

Although limited laboratory testing showed the feasibility of using the Webb type system for direct, continuous monitoring of beryllium, considerable difficulty was encountered in field tests (power plant) with a prototype, continuous monitor for measuring beryllium directly in stack effluent. However, the Webb arc emission spectroscopic system still remains the most promising approach to monitoring trace metal in work environments and in effluent from stationary sources. The advantages are: (a) direct, real time, continuous measurements down to low trace levels (1 $\mu g\ Be/m^3$); (b) specificity; (c) moderate volume flow rate (up to 40 l/min); and (d) relatively simple low weight instrument package. Lower detection limits <<1 $\mu g\ Be/m^3$ can be obtained by integrating the emission signal for 30-60 seconds, resulting in sampling and analysis times of approximately 30-90 seconds. For beryllium, the analytical working range by direct measurement without signal integration is 1 μg - 200 $\mu g\ Be/m^3$. Problems to be solved include: (a) fouling of the electrodes and cell with particulate deposits when monitoring stack effluents having high loadings of refractory (silicate) particulate, and (b) absorption of moisture and other stack gases by the asbestos cell resulting in a breakdown of electrical insulation.

For stationary emission sources, yielding relatively high loadings of refractory silicate particulate (>1000 μg/m³), a much hotter vaporization system other than the Webb cell design is needed. In the Webb cell, the relatively small arc zone serves to vaporize the particulate and to induce optical emission spectra but does not have sufficient energy to accomplish both simultaneously and efficiently. Solutions to this problem would involve either the addition of a vaporizing system immediately prior to the analytical arc discharge or the use of a hotter analytical discharge system. In the former case, an auxiliary arc could be used to vaporize the particulate prior to the analytical arc. With the latter approach, a hotter excitation system - radio-frequency induced plasma or Shumaker arc oven - would be used.

2.4 Conclusions

2.4.1 Beryllium and Cadmium Monitor

At the present state-of-the-art, there is no analytical technique available for universal application as a direct, continuous, monitor of beryllium and cadmium from all types of stationary source emissions at the A.C.G.I.H. 1967-TLV levels of 0.002 mg Be/m³ and 0.02 mg Cd/m³ (as soluble salts and metal dust) or 0.1 mg Cd/m³ (as CdO fume).

The Webb system (ref. 1,2) can be used for Be monitoring in a limited number of situations, where the total particulate loading is low (<1000 μg/m³) and where Be is present in excess of 0.1 μg/m³.

Although several possible solutions to the air effect problem with RF induced plasma can be suggested, considerable development work would be required to establish feasibility. Also, the cost and time factors, and the dilution effects for the actual monitoring measurements may become excessive. Possible approaches include removal of oxygen or reaction of oxygen to form relatively stable oxide (CO, CO_2, H_2O, or metal oxide) and incorporation of additives to inhibit nitrogen-oxygen free radical reactions and metal-oxygen compound formation, or to change the ionization potential in selected plasma zones. An alternate approach would rely on spectral measurements of metal oxide emission bands or spectral lines characteristic of more energetic transitions.

After reviewing the results obtained with the radio-frequency induced plasma and after discussion with Drs. V. A. Fassel (Iowa State University), T. B. Reed (MIT), and R. Mavrodineanu (NBS), we have concluded that a radio-frequency induced total air plasma or an argon plasma with moderate percentage of air which will provide for detecting trace quantities of cadmium in air may be attainable eventually, but not at the present state-of-the-art.

For the Webb cell system to be usable under conditions of higher particulate loadings, particularly in systems containing refractory silicates, an additional source of energy is needed to vaporize the particulate.

Possible approaches include using a DC arc or RF plasma to preheat the sample prior to the Webb cell. An alternate approach would be to use a Shumaker arc chamber (see Section 6.0), which develops high temperatures (>13,000°K), in place of the Webb cell.

2.4.2 Analytical Technology - Determination of Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium, Copper, Lead, Manganese, Mercury, Nickel and Vanadium

A number of analytical approaches can be used to determine each of the subject elements. Most techniques, however, rely on collecting an integrated sample by filtration or by isolation in impinger fluids. As a consequence, errors resulting from losses of volatile species can be serious. Despite difficulties encountered in this program in attempting to measure beryllium and cadmium emissions from a power plant source, spectroscopic techniques (emission and atomic absorption) remain the more promising approaches to monitoring a wide variety of trace metals directly.

The Webb arc system used in Task I of this program for detecting Be can be applied to monitoring other elements. Limits for other elements need to be defined. The major disadvantage occurs when handling stack effluents having heavy loadings of refractory particulate. Modification of the Webb system to produce a hotter vaporizing source is needed.

With selected stationary emission sources, and under the proper environmental conditions, analytical techniques limited to specific elements can be used. For example, in situations where the total particulate loading is extremely low and the particulate consists of mostly beryllium and/or its compounds, a continuous monitoring system for beryllium based on using a sintered metal filter impregnated with an alpha emitter to produce the reaction

$$^{9}\text{Be} + \alpha \rightarrow n + \gamma + {}^{12}\text{C}$$

can be used (see Appendix II, Section 4.4). Also, with mercury or its compounds, a mercury reduction process (chemical or pyrolytic) coupled with a photometric measurement can yield a rapid, intermittent determination (see Appendix III, Section 3.1). For organic lead compounds, reduction over hot carbon followed by atomic absorption measurements of the atomic lead can be used for continuous monitoring; however, application to effluent containing high loadings of inorganic particulate is questionable (see Appendix IV, Section 3.2).

By using collection devices (filters and impinger fluid), analyses of heavy metals, but not Be and B, can be made with XRF techniques. The major limitations are matrix interferences, time, and potential loss of "volatile" compounds.

2.5 Recommendations

Based on the laboratory and field studies reported by Webb et al. (ref. 1,2) for monitoring Be in work environments, and the laboratory data obtained in this program, which substantiate Webb's observations, we recommend that a program based on a modified Webb-type approach be continued. The applicability of the system to direct, continuous monitoring of Be and Cd, as well as other, potentially toxic, metals must be better defined. The system could also be used at the effluent side of a standard EPA sampling train to verify the efficiency of the EPA sampling procedure.

The following program is suggested:

1. Test a Webb arc chamber and pulsed DC arc electronic system on a low level Be emission source, e.g., Be machining or refining operation.
2. Modify a Webb arc chamber by incorporating auxiliary electrodes and additional chamber heating and determine feasibility of further applying the system to stack emissions containing relatively high loadings of particulate (power plants and incinerators).
3. Modify electronics and optical system to provide modulation capability to enhance discrimination of analytical signal from background. Wavelength modulation and use of lock-in amplifier system is suggested.
4. Establish feasibility of using a hotter arc chamber of the Shumaker type to vaporize particulate in stack gases with high loadings.
5. Determine feasibility in laboratory studies of using the arc excited emission spectroscopic technique as a universal, direct, continuous monitor for measuring Be, Cd, B, Ba, Cr, Cu, As, Sb, Pb, Ni, Mn, Hg, and V.
6. Interface a Webb arc chamber with a standard EPA sampling train to validate the efficiency of the collection methods (based on filters and impingers) for total particulate, and for beryllium, lead, and other toxic materials.

3. LITERATURE SURVEY AND BRIEFING DOCUMENTS

Detailed briefing documents describing technology appropriate to the analytical problem of continuous measurement of beryllium, cadmium, mercury, lead, arsenic, antimony, barium, boron, chromium, copper, manganese, nickel, and vanadium are presented as five appendices to this report. Data for the most promising techniques in these documents are summarized in Tables I-XII. Whenever possible, data derived from a known, specific application are listed. Also, the tables are based on data for systems that would be practical as continuous, or moderately intermittent, monitors for stationary source emissions. In some cases, lower detection limits are attainable with highly sophisticated laboratory research instrumentation, e.g., Van de Graaff generator for x-ray emission (fluorescence) spectroscopy, but these devices are impractical for field monitoring. Due to lack of detailed information appearing in the available literature some data had to be supplemented by crude estimates.

At this time, there is no method available that can be immediately adapted to monitoring particulate, fume and/or gaseous emissions from stationary sources for trace quantities of Be, Cd, Hg, Pb, As, Sb, Ba, B, Cr, Cu, Mn, Ni, and V on a continuous, 24-hour basis. A number of techniques have been applied to measuring selected elements from this group in specific chemical or physical forms in work environment or ambient air, but no technique has been applied to all of the listed elements in the variety of chemical or physical forms that can be encountered from stationary source emissions.

It is important to understand that at the current state-of-the-art most of the methods described in the briefing documents have not been applied to the continuous monitoring of trace elements in air or in stack gas emissions. The methods cited in the briefing documents and summarized in Tables I-XII are presented primarily to provide background information for the selection of potential avenues, where R&D efforts may best be applied. Some of the information listed in Tables I-XII was derived from the analysis of aqueous samples (atomic absorption spectrophotometry) and geologic specimens (alpha particle scattering measurements of moon specimens). As a consequence, the detection limits quoted in the original publications and presented in the summary tables are in a variety of units. These and other techniques can be applied to determinations of trace elements, if specimens are collected on filters or in impinger fluids and analyzed directly or after suitable chemical transformation. Since the "detection level" depends on so many factors including: volume of air sampled, size or volume of the collection device, surface area or volume of sample exposed to the measuring system (XRF, alpha particle scattering), and composition of sample matrix, we chose not to introduce a possible bias by adjusting the literature detection level to a common unit. The values reported in the summary tables are those presented in the original reports and merely serve to acquaint the reader with the potential application of the method.

A major concern in all of the candidate analytical approaches is the problem related to obtaining a representative sample without loss of the element sought or without producing changes in the chemical composition which would affect the precision or accuracy of the analytical measurement. Techniques based on analyzing specimens collected on filters may yield erroneous results due to losses of sample through volatilization of particulate from the filter during the sampling processes or due to inability to collect fume or gaseous metal compounds.

Any technique relying on the collection of particulate on filters from relatively large volumes of air over a lengthy time period (1-24 hrs) risks the potential loss of volatile compounds. This is true even with relatively nonvolatile compounds depending on the gas temperature and composition. BeO vaporization can be enhanced and promoted at lower temperatures by a gas composition containing appreciable amounts of water; Cr_2O_3 evaporation is enhanced in an oxygen atmosphere containing water vapor; $PbCl_2$ volatilization is increased significantly at lower temperatures in a stream of HCl (see Appendix I, Section 2).

PbO vaporizes at red heat, but is stabilized in presence of silica and/or iron oxide. PbS volatilization occurs at normal stack temperatures and is promoted by currents of combustion gases in metallurgical furnaces. Evaporation losses of mercury compounds and arsenic trioxide can occur at ambient temperatures.

The most attractive candidate analytical techniques are based on spectroscopic measurements taken from the excitation of continuous, flowing effluent (ref. 1-7). These techniques do not require the collecting of particulate and thus are not affected by the problems associated with isolating specimens on filters or in impinger fluids. By using a spectroscopic analysis of a continuous flowing system, measurements of total element concentration as particulate, fume, and vapor are attainable in sampling and analysis time periods of 60 seconds.

Summaries of the briefing documents (Appendices II-VI) identifying the analytical technology for continuous monitoring of Be, Cd, Hg, Pb, As, Sb, Ba, B, Cr, Cu, Mn, Ni, and V are presented in the following sub-sections. Tables I-XII show the summary data for some of the analytical techniques considered as potential candidate methods.

3.1 Summary - Analytical Technology for Continuous Monitoring of Beryllium and Cadmium

There is no method available at this time that can be immediately adapted to monitoring particulate and/or fume emission from stationary sources for beryllium and/or cadmium on a continuous, round-the-clock basis. The work of Webb, et al. (Appendix II, Section 4.1.1) suggests that a continuous monitor can be developed based on emission spectroscopic measurements of a continuous flowing stream (40 liters/minute) of stack gases. This type of emission spectroscopic measurement can provide a means of monitoring both beryllium and cadmium (or most other metallic elements and some non-metals) simultaneously. The technique has the necessary (a) selectivity, (b) speed (30 sec.) for rapid, repeated analysis, and (c) sensitivity ($\sim 1\ \mu g/m^3$).

An evaluation of the emission spectrographic approach must be made to establish the efficiency of the excitation process when analyzing entrained particulate of variable particle size and when measuring stack emissions having moderate to high loadings of entrained particulate. The Webb system worked well in monitoring the beryllium content in a work environment where the particulate was principally beryllium compounds. No data are available regarding performance in measuring small amounts (1-100 ppm) of Be or Cd in inorganic particulate, e.g., fly ash.

Electrode wear and deposition of particulate from stack gases having high loadings of particulate relative to ambient or work-place atmospheres may be major problems in applying the Webb technique to monitoring stack emissions. By using an electrodeless discharge system (radio-frequency coupled excitation), the electrode wear and deposition problems could be eliminated or minimized.

The major problem related to using radio-frequency excitation is the difficulty in initiating and maintaining an air plasma of desirable geometry. Also, adverse oxidation effects may limit the sensitivity. By blending mixtures of inert matrix gas (A or He) with air containing entrained particulate and with a reducing gas, e.g., hydrogen, a stable plasma and suitable sensitivity may be attained. However, by diluting the sample with an inert or a reducing gas, some loss in the capability to detect the lower concentrations of Be or Cd will be experienced.

X-ray fluorescence techniques can be used for measuring cadmium, but not for determining beryllium. X-ray tube excitation sources have been applied to analyses for cadmium, but limited work has been performed with radioisotope induced x-ray emission (^{241}Am). The application of radioisotope induced x-ray emission spectroscopy to determining cadmium in collected stack emission particulate may require further development of new or modified radioisotope sources, e.g., ^{125}I.

A trade-off of performance specifications may depend on the type of emission source being tested. The Webb system may be usable for low (1-100 $\mu g/m^3$) Be or Cd levels in source emissions composed of particulate or fume having Be or Cd as major components and little, if any, other metallic elements. Similarly, the method based on the $^9Be(\alpha,n,\gamma)^{12}C$ reaction (Appendix II, Section 4.4.5) can be used for measuring beryllium continuously in atmospheres or stack gas emissions containing principally beryllium or its compounds down to 1 $\mu g/m^3$, but cannot be used where non-beryllium particulate would be excessive.

3.2 Summary - Analytical Technology for Continuous Monitoring of Mercury

At this time, there is no continuous monitoring system which measures total mercury (vapor and particulate) directly. Most monitors are based on the measurements of mercury vapor alone.

The techniques (Appendix III) which have sufficient specificity and sensitivity are:

(a) mercury vapor photometry (non-flame atomic absorption)

(b) microwave induced emission spectroscopy

(c) arc excited or radio-frequency induced emission spectroscopy.

Mercury vapor photometry measures elemental mercury vapor only and would require a pretreatment step to generate elemental mercury from chemically bound mercury. Also, the technique is subject to interferences from organic compounds, smoke, dust, etc. As a consequence, a compensation technique or removal (physical or chemical) of the interfering materials must be made.

When using low wattage microwave induced emission spectroscopy, a pretreatment step to vaporize particulate or to reduce chemically bound mercury to elemental mercury vapor must be used. The microwave energy (low power) is not sufficient to vaporize particulate directly.

With arc excited or radio-frequency induced emission spectroscopy, sufficient energy is generally available to vaporize particulate up to particle sizes of approximately 80μ at flow rates of 40 liters/minute.

Preheating of the chemically bound mercury to generate and vaporize elemental mercury can be accomplished by induction or resistance heating, oxy-hydrogen or oxy-acetylene flame, ac-dc arc, or rf-plasma.

For each of the techniques measuring emission spectra, sufficient spectral resolution with a monochromator must be available

Table I-A

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR BERYLLIUM
(Based on Literature Review)

Evaluation Parameter	Emission Spectroscopy			Atomic Absorption[1]		X-ray Emission (Fluorescence)
	Arc & Spark Excitation	Induction Coupled		Conventional Flame	Flameless	
		Radiofrequency	Microwave			
Specificity	High	High	High	High	High	
Detection Limit	0.5 $\mu g/m^3$	0.1 ppm in solid MgO	Est. 10^{-12}–10^{-10}g	0.03 ppm in H_2O	9 x 10^{-13}g	
Range	0.5-100 $\mu g/m^3$	0.1-500 ppm	10^{-12}–10^{-7}g	0.03 to 4 ppm	Not determined	
Accuracy	Est. 5-10%	Est. 5-10%	Est. 5-10%	-	-	
Precision	5-10%	6.5% @ 10 ppm	7% @ 10^{-10}g 40% @ det. limit	2%	>2%	
Operational Mode	Continuous or intermittent	Continuous or intermittent	Intermittent anal. collected specimen	Generally solution	Generally solution	Not applicable due to low energy of Be X-rays
Sampling Time[2]	20 sec.	20-60 sec.	10 min-24 hrs	10 min-24 hrs	10 min-24 hrs	
Analysis Time	60 sec.	*ca*. 60 sec.	<2 min.	30 min.	30 min.	
Total Cycle Time	75 sec.	*ca*. 1-2 min.	12 min-24 hrs	1 hr-24 hrs	1 hr-24 hrs	
Calibration Technique	(a) Std.aerosol (b) Be-Cu electrode	Dry, powdered beryllium carbonate in MgO	Std. samples (solution or aerosol)	Std. solutions	Std. solutions	
Sample Form	Air specimen	Particulate (MgO) in argon	Collected particulate or solution	Aqueous solution	Aqueous solution	
Interferences	Possibly slight H_2O, Hg & particle size	None reported	Matrix, total mass & memory effects	Refractory nature of Be	Refractory nature of Be	
Unit Output	$\mu g/m^3$	ppm Be in MgO	μg	μg	μg	
Special Equip.	None		Vacuum	None	None	
Multi-element Application	Yes	Yes	Yes	Depends on choice of lamp & flame temp.	Depends on lamp choice	
Safety Hazard	High electrical voltages	High electrical voltage & flame	Flame	Open flame	Moderate eleccrical voltages	
Problem Areas	Electrode deterioration	Possible mass overloading of plasma	Matrix; total mass overloading; memory effect	Refractory nature of Be	Refractory nature of Be; coating effect	
Routine Maintenance	Adjust electrodes every 8 hrs	Very little	Clean excitor tube every few hours	High consumption of fuel gases	Clean tube regularly	
Volume Flow Rate	40 l./min.	ca. 500 cc/min.	-	-	-	
Est. Instrument Cost[3]	$10,000-20,000	$10,000-20,000	$10,000-20,000	$5,000-10,000	$10,000-15,000	
Est. Instrument Size[4]	3' x 2' x 6' 100-500 lbs	4' x 2' x 6'	4' x 2' x 6'	4' x 2' x 6'	4' x 2' x 6'	
Compatibility w/Cd	Yes	Yes	Yes (Depending on method of vaporizing Be)	Each needs different flame temperature	Yes	

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[1] Atomic absorption mode could be used with RF excitation. Multi-element functionality would be restricted by number of elements in lamp or lamps.

[2] If collection device is required, sampling time depends on level of Be in the specimen and the sensitivity of the analytical technique.

[3,4] Cost and size mostly dependent on electronics or dispersion system (monochromator) and can be minimized with proper design criteria.

[5] Requires chemical separation to eliminate interference.

[6] General sensitivity (not detectable directly on air particulate sample).

[7] Mounted on pick-up truck.

Table I-B

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR BERYLLIUM

Evaluation Parameter	Activation Analysis			Alpha-Particle Scattering	Mass Spectrography
	Neutron		Radioisotope Photo-activation		
	Reactor	Radioisotope			
Specificity	Poor[5]	Poor[5]	High	Moderate	Interference from $^{27}Al^{+3}$
Detection Limit	~15 µg[6]	~15 µg[6]	2 $\mu g/m^3$	1 $\mu g/cm^2$	Est. ~0.01 $\mu g/m^3$
Range	(??)	(??)	2-25 $\mu g/m^3$	1-150 $\mu g/cm^2$	0.004 $\mu g/m^3$ to 40 $\mu g/m^3$
Accuracy	(??)	(??)	(??)	1 atomic %	Semi-quantitative
Precision	2-10%	2-10%	40% @ 25 µg w/2 min. counts	No data	Semi-quantitative
Operational Mode	Intermittent Anal. Filter	Intermittent Anal. Filter	Intermittent Anal. Filter	Intermittent Anal. Filter	Intermittent Anal. Filter
Sampling Time-	10 min-24 hrs	10 min-24 hrs	2 min @ 25 $\mu g/m^3$	10 min-24 hrs	1 hr-24 hrs
Analysis Time	Lengthy, requires sep.	Lengthy, requires sep.	2 min @ 25 $\mu g/m^3$	20-2453 min	2-1/2 hrs
Total Cycle Time	~2-8 hrs	~2-8 hrs	4 min @ 25 $\mu g/m^3$	1 day	3-24 hrs
Calibration Technique	Std. samples	Std. samples	Std. samples	Data for pure elements	Std. samples
Sample Form	Particulate on filter	Particulate on filter	Particulate on filter tape	Particulate on filter paper	Particulate extracted from filter
Interferences	Elements w/high cross-sections	Elements w/high cross sections	Background from source	Sample surface thickness & particle size	$^{16}O^{-2}$; $^{27}Al^{-1}$
Unit Output	µg	µg	$\mu g/m^3$	Atomic % or µg	µg
Special Equip.	Nuclear reactor & shielding	Shielding	Radioactivity shielding	Radioactivity shielding & vacuum	Vacuum
Multi-element Application	Yes with exceptions	Yes with exceptions	No	Boron to titanium	Yes
Safety Hazard	Radioactivity	Radioactivity	Radioactivity leakage	Radioactivity leakage	Moderate electrical voltages
Problem Areas	Reactor mass unacceptable	Radioactivity leakage	Leakage of source	Leakage of source and maint. vacuum	Semi-quantitative & O or Al interferences
Routine Maintenance	-	Very little	Check covering on source daily	Maint. vacuum and source	Maint. vacuum
Volume Flow Rate	-	-	79 l./min	-	-
Est. Instrument Cost[3]	>$100,000	$25,000-50,000	Parts - $5,000 Labor - $5,000	Est. $10,000-20,000	ca. $100,000
Est. Instrument Size[4]	Massive	Heavy, but mobile[7]	Unknown, Est. 2' x 4' x 6'	Head - 13.3 cm x 17.1 cm x 11.7 cm (<4 kg)	Not mobile
Compatibility w/Cd	Requires chem. separation	Requires chem. separation	No	No	Yes

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[1] Atomic absorption mode could be used with RF excitation. Multi-element functionality would be restricted by number of elements in lamp or lamps.

[2] If collection device is required, sampling time depends on level of Be in the specimen and the sensitivity of the analytical technique.

[3,4] Cost and size mostly dependent on electronics or dispersion system (monochromator) and can be minimized with proper design criteria.

[5] Requires chemical separation to eliminate interference.

[6] General sensitivity (not detectable directly on air particulate sample).

[7] Mounted on pick-up truck.

Table II-A

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR CADMIUM
(Based on Literature Review)

Evaluation Parameter	Emission Spectroscopy			Atomic Absorption[3]		X-ray Emission (Fluorescence)
	Arc & Spark Excitation[1]	Induction Coupled		Conventional Flame[2]	Flameless	
		Radiofrequency	Microwave			
Specificity	High		High	High		Good
Detection Limit	ca. 0.1 µg		2.0 x 10^{-11}g	0.005 mg/m³	Same as Be - Table I	0.001% (~0.5 µg)
Range	0.1-100 µg		2.0 x 10^{-13}g to 5.0 x 10^{-10}	0.02 mg/m³ to 0.2 mg/m³		>0.001%
Accuracy	No data		Insufficient data	No data		No data
Precision	±25% @ 3 µg level	Estimated to be similar to Be - Table I	10% @ 2.5 x 10^{-11}g	±10-15%		-
Operational Mode	Intermittent Anal. filter		Cd in solution	Continuous		Intermittent Anal. filter
Sampling Time[4]	10 min-24 hrs		10 min-24 hrs	Immediate		10 min-24 hrs
Analysis Time	5 min		<2 min	Immediate		10 min-1 hr
Calibration Technique	Std. solutions added to filter.		Std. soltuions	Std. solutions		Std. samples
Sample Form	Particulate on filter		Cd in H_2O; evaporated from filament	Air sample		Particulate on on filter
Interferences	Particle size, self-absorption		V; As; selective volatility may occur on filament	Particle size material - >1 micron	Particle size	Matrix; Particle size; thickness; inter-element; A; blanks
Unit Output	µg		µg or µg/ml	mg/m³		µg
Special Equip.	Special electrode system		Vacuum system	Propane blow lamp		Vacuum or helium purge
Multi-element Application	Yes		Yes	Pb		Atomic number >11
Safety Hazard	High electrical voltages		Flame type excitation	Flame		X-rays or radioactivity
Problem Areas	Handling the filter		Mass overloading of plasma	Particle size	Particle size	Matrix; particle size interferences
Routine Maintenance	Adjustment and changing of electrodes		Clean excitor tube regularly	Replace propane - 2 hrs; batteries - 20 hrs		Leak check sample chamber regularly or replace He cyl.
Volume Flow Rate	0.5 ft³/min		-	Comparable to human respiration		-
Est. Instrument Cost[5]	approx. $50,000		$10,000-20,000	~$5,000		$10,000-30,000
Est. Instrument Size[6]	approx. 4' x 2' x 6'		approx. 4' x 2' x 6'	(a) 40 cm x 25 cm x 15 cm (b) 45 cm x 27 cm x 13 cm 25 kg		approx. 4' x 2' x 6'
Compatibility w/Be	Yes		Yes	No		No

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[1] Based on direct analysis of filter paper with special spark electrode system and direct reading Baird-Atomic spectrograph. Continuous monitoring arc technique used for Be (Table I) could also be used for Cd.

[2] Data for special continuous monitoring system.

[3] Atomic absorption mode could be used with RF excitation rather than conventional flame if ionization is not too great.

[4] If collection device is required, sampling time depends on level of Be in the specimen and the sensitivity of the analytical technique.

[5],[6] Cost and size mostly dependent on electronic or dispersion system (monochromator) and can be minimised with proper design criteria.

[7] General sensitivity. On air particulate samples, levels below 9.6 µg cannot be measured without radiochemical separation to eliminate interferences.

Table II-B

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR CADMIUM

Evaluation Parameter	Activation Analysis			Alpha-Particle Scattering	Mass Spectrography
	Neutron		Radioisotope Photo-activation		
	Reactor	Radioisotope			
Specificity	Barely adequate	Barely adequate			Good
Detection Limit	0.005 μg[7]	0.005 μg[7]			0.3 ppm
Range					>0.3 ppm
Accuracy					Semi-quantitative
Precision					Semi-quantitative
Operational Mode			Not applicable to cadmium	Not applicable to cadmium	Intermittent anal. filter
Sampling Time[4]	Same as Be - Table I	Same as Be - Table I			1 hr-24 hrs
Analysis Time					3 hrs-24 hrs
Calibration Technique					Std. samples
Sample Form					Particulate extracted from filter
Interferences					None reported
Unit Output					ppm or μg
Special Equip.					Vacuum
Multi-element Application					Yes
Safety Hazard					Moderate electrical voltages
Problem Areas					Semi-quantitative
Routine Maintenance					Maintain vacuum
Volume Flow Rate					-
Est. Instrument Cost[5]					ca. $100,000
Est. Instrument Size[6]		Heavy, but mobile			Not mobile
Compatibility w/Be	Requires chem. separation	Requires chem. separation			Yes

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[1] Based on direct analysis of filter paper with special spark electrode system and direct reading Baird-Atomic spectrograph. Continuous monitoring arc technique used for Be (Table I) could also be used for Cd.

[2] Data for special continuous monitoring system.

[3] Atomic absorption mode could be used with RF excitation rather than conventional flame if ionization is not too great.

[4] If collection device is required, sampling time depends on level of Be in the specimen and the sensitivity of the analytical technique.

[5,6] Cost and size mostly dependent on electronic or dispersion system (monochromator) and can be minimized with proper design criteria.

[7] General sensitivity. On air particulate samples, levels below 9.6 μg cannot be measured without radiochemical separation to eliminate interferences.

to provide separation of spectral interferences which may arise from the matrix. The mercury vapor photometer system does not necessarily use a monochromator, since the basis of the technique (atomic absorption phenomenon) provides specificity for mercury.

The need for a monochromator in the emission spectroscopy techniques, particularly the low power microwave induced optical emission, can be eliminated if collection-desorption as a gold or silver amalgam is used to isolate the mercury from interfering components of the matrix.

Detection of mercury vapor with an argon ionization system can be accomplished on a short-term, intermittent basis if the bound mercury is decomposed to mercury vapor and the mercury vapor is removed from the matrix with silver or gold amalgamation. Desorption of elemental mercury vapor into the argon ionization detector would produce a highly responsive signal.

Five systems can be identified for potential use as continuous monitors for total mercury in stationary source emissions.

System A

Sample → Thermal decomposition → Compensated mercury vapor photometer

System B

Sample → Thermal decomposition → Isolation as gold amalgams → Mercury vapor photometer

System C

Sample → Thermal decomposition → Isolation as gold amalgam → Microwave induced emission spectroscopy

System D

Sample → Radio-frequency induced or arc excited emission spectroscopy

System E

Sample → Thermal decomposition → Isolation on carbon or as gold amalgam → Argon ionization detection

Although System D does not require a separate thermal decomposition sub-system, it does require a relatively good monochromator to provide spectral resolution. However, with the monochromator, System D provides for multi-element monitoring.

Systems A, B, and C are more sensitive than System D, but require high efficiencies in the thermal decomposition and isolation steps (when needed as in B and C). No information is available on decomposition efficiencies of refractory particulate matrices or at modest to high flow rates. Also, little information is reported on amalgamation and desorption efficiencies of mercury on gold at modest to high flow rates.

3.3 Summary - Analytical Technology for Continuous Monitoring of Lead

Although several techniques have been applied to the continuous monitoring of lead vapor, principally as the organo-lead compounds, no single method has been tested completely to qualify as a continuous monitor for total lead, i.e., vapor and particulate, from stationary source emissions.

Non-flame atomic absorption spectroscopy, preceded by a thermal and/or chemical reaction decomposition step to reduce airborne lead compounds to elemental lead and to maintain the elemental lead as vapor, should be considered. The major problems in adapting the most effective decomposition system (passage of air containing lead compounds over hot carbon) used for ambient air are: (a) efficiency of the reducing reaction at high stream velocities normally encountered in stack emissions and at the resulting short residence time in the decomposition zone is unknown; (b) potential plugging by refractory particulate in the carbon chamber when used with stack emissions involving high non-lead content, e.g., power plant fly ash, needs to be evaluated; and (c) consumption of the hot carbon rods at high stack gas flow rates, where the stack gases are predominantly oxidants, e.g., oxygen, etc., must be determined.

Continuous monitoring of ambient air flowing at 1 ft^3/min. has been accomplished by emission spectroscopy with a spark discharge. The technique permits a working range of 0.003 mg Pb/ft^3 to 0.05 mg Pb/ft^3, but based on newer instrumentation may allow lower limits. The instrumentation was applied to measuring lead in vapor and particulate. Other methods of excitation - rf plasma, and intermittent arc - may also improve the efficiency of the emission spectrographic method.

X-ray emission (fluorescence) spectroscopy can be applied to measuring lead in particulate collected on filters. The major restriction to its application for determining total lead is its inability to analyze vapor. Some means must be found to collect volatile lead compounds on a filter-type media. Some consideration should be given to adapting paper tape samplers impregnated with complexing agents, e.g., tetrahydroxy-p-benzoquinone, used in collecting lead fume for colorimetric analyses.

Table III

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR MERCURY
(Based on Literature Review)

Evaluation Parameter	Mercury Vapor Photometer (Flameless Atomic Absorption)	Flame Atomic Absorption and Fluorescence		Emission Spectroscopy		Radioisotopic Method
		Absorption	Fluorescence	Radio-Frequency or Arc Excitation[e]	Microwave (Low Power)	
Specificity	Good	Good (except for high Co matrix)	Good	Good	Good	Good
Detection Limit	1-10 $\mu g/m^3$[a] (0.0003 μg)	(a) 1-10 $\mu g/ml$ (H_2O) (b) 0.002 μg/liter of air (carbon)	(a) 0.08 $\mu g/ml$ (direct) (b) 0.002 $\mu g/ml$ (additives)	Est. 10^{-9}-10^{-10}g	<1 x 10^{-10}g[f]	0.01 $\mu g/l$
Range	Depends on path length, etc. (See Appendix III)	1-300 $\mu g/ml$ (H_2O)	-	-	Linear - 0.1-100 ng as methylmercuric chloride	0.01 - 1.2 $\mu g/l$
Accuracy	Insufficient data	Rel. Error - ≤10%	Rel. Error - ≤10%	Data inadequate (Est ±10%)	Data inadequate (Est ±10%)	Insufficient data
Precision	Std. dev. @ 0.0003 μg - 37% " " @ 0.01 μg - 3 to 8%	Coeff. of variation 0.5-2%	Approx. same as AA	Data inadequate (Est ±10%)	Data inadequate (Est ±10%)	Std. dev. 0.004 $\mu g/l$ (range 0.01-0.02 $\mu g/l$) and 0.075 $\mu g/l$ (range 0. [illegible] 1.2 $\mu g/l$)
Operation Mode	Continuous or intermittent	Intermittent	Intermittent	Continuous or intermittent	Intermittent	Intermittent
Sampling Time	Continuous (no time delay)	10 min - 2 hrs	10 min - 2 hrs	Approx. 1 min.	Approx. 1-10 min.	2-20 min.
Analysis Time	Almost instantaneous	Approx. 15 min.	Approx. 15 min.	Approx. 1 min.	Approx. 2-5 min.	Counting time-100 sec
Total Cycle Time	Almost instantaneous	25 min - 2-1/2 hrs	25 min - 2-1/2 hrs	Approx. 2 min.	Approx. 3-15 min.	5-25 min.
Calibration Technique	Std. samples Hg vapor	Std. solutions	Std. solutions	Std. solutions	Hg^0 vapor or Hg salts on heated probe	Air saturated with Hg vapor
Sample Form	Elemental Hg vapor[b]	(a) Hg vapor or reactive particulate in H_2O (b) Hg vapor or particulate on carbon	Hg vapor or reactive particulate in H_2O	Hg^0 vapor + particulate	Hg^0 vapor only	Hg vapor
Interferences	Organics, ozone, particulate, sulfides, magnetic fields	Spectral - Co Chemical - Oxidizing & reducing reagent	S^{2-}, Au, Pt, Cr(VI), Ag	-	Matrix, total mass	Sulfide ion
Unit Output	$\mu g/m^3$ or μg	$\mu g/ml$ or ppm	$\mu g/ml$ or ppm	Mass or mass/volume	μg	Counts/100 sec. convertible to μg or $\mu g/l$
Special Equip.	[c]	(a) - (b) Carbon collector & tantalum boat	-	-	Vacuum	Radioactive isotope and shielding
Multi-element Application	Hg[d]	Yes, with lamp & flame limitations	Yes, with limitations	Yes	Yes (with monochromator)	Specific for Hg, but absorber could be modified for other volumetric elements having radioactive isotopes
Safety Hazard	Moderate electrical voltages Toxicity of Hg	Open hot flame	Open hot flame	Flame-like discharge or high voltage electrical discharge	Flame-like discharge	Moderate radioactivity
Problem Areas	Spectral interferences; inability to do particulate directly; magnetic interferences	Co interference Presence of oxid. & red. agents. Distribution of Hg(I), Hg(II) and Hg^0	Chemical interferences	Particle size	Must collect mercury; must decompose particulate	Sulfide and depletion of Hopcalite
Routine maintenance	Very little	Replace burner gases	Replace burner gases	RF-replace carrier gas (A or He) ca. 300 cc/min (RF)	Clean excitor tube, replace carrier gas supply	Replace isotope exchange solution and Hopcalite
Volume Flow Rate	No major limitation	-	-	Up to 40 l/min (arc)	Depends on efficiency of collection system	0.5 to 1.5 l/min
Est. Instrument Cost	$500 - $5,000	$2,000 - $10,000	$2,000 - $10,000	$10,000 - $20,000	$10,000 - $20,000	$5,000 - $10,000
Est. Instrument Size	Portable - approx. 1' x 1' x 0.7' (17 lbs) to approx. 2' x 4' x 6'	2' x 4' x 6'	2' x 4' x 6'	4' x 2' x 6'	4' x 2' x 6'	4' x 2' x 6'

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[a] Depends on optical path, electronics, instrument design, collection medium (if used), and compensation technique for background.

[b] If decomposition step is used, a pretreatment can measure total Hg (vapor and particulate).

[c] Thermal decomposition and isolation steps can be used to yield total Hg and minimize interferences.

[d] System specific for Hg, but non-flame atomic absorption phenomena could be used on other elements.

[e] Based on continuous flow system (Appendix III, ref. 25,26,27).

[f] Based on data from Appendix III, ref. 28. MRC preliminary data indicates potential detection limit 10^{-12} to 10^{-14}g.

When using the most sensitive lead line (L_α) for measuring lead by x-ray emission (fluorescence) spectroscopy, the analyst must be aware of potential spectral interference from As (K_α) in media containing moderate amounts of arsenic. The PbL_β line has been used successfully with ^{109}Cd radiosiotope excitation.

Techniques using γ-absorptimetry are not necessarily adaptable to universal measurement of lead but could be used in special circumstances where lead or its compounds would be the only compounds emitted and could be collected on filters, etc. The sensitivity of the method needs to be optimized and specific detection limits established.

3.4 Summary - Analytical Technology for Continuous Monitoring of Arsenic and Antimony

There is no technique available for measuring arsenic and antimony continuously in ambient air or in stack emission. All techniques presently used in measuring the air pollutants - arsenic and antimony - require the collection of particulate in impingers or on filters.

The low sublimation temperature of As_2O_3 suggests the potential loss of volatile arsenic compounds from particulate collected on high volume filtering systems. Analytical techniques, e.g., x-ray emission (fluorescence) spectroscopy, neutron activation analysis, and mass spectroscopy, using this method of collection may yield low results.

Similar low results will also be observed with emission spectrographic techniques based on analyzing particulate collected on filters. However, emission spectrographic techniques based on the excitation of a continuous flowing stream of air or stack gas through an excitation zone would not have this problem.

Other than using flame (acetylene-oxygen), or radio-frequency induced excitation of flowing solutions of arsenic and antimony, no data are available regarding spectrographic analyses of flowing air samples. Based on information derived from flame excitation studies, a moderate amount of development work should be anticipated to establish the optimum viewing zone in the flame or plasma. Emission lines of elements (arsenic and antimony) of high excitation potential and high ionization potential may not appear in the flame mantle, but occur as intense emission lines in the reaction zone under the proper conditions (see Appendix V, Section 3.3). The use of radio-frequency or microwave-induced plasmas should be considered. The latter when used in a low power mode will not permit direct measurements, but will require isolation of the arsenic or antimony in impinger solutions.

Table IV

SUMMARY OF EVALUATION PARAMETERS FOR CONTINUOUS MONITORING SYSTEM FOR LEAD
(Based on Literature Review)

Evaluation Parameter	Emission Spectroscopy (Spark Excitation)	Non-flame Atomic Absorption	X-Ray Emission (Fluorescence) Spectroscopy (X-ray Tube Excitation)
Specificity	Good	Yes	Yes
Detection Limit	<0.003 mg/ft³	0.16 μg/m³	0.05 μg/m³
Range	0.003 mg/ft³-0.05 mg/ft³	0.16 μg/m³-54 μg/m³	Dependent on matrix effects, (1 μg/cm² up to 1.5 mg/cm² on filter)
Accuracy	No data (Est. ±10%)	Insufficient data	Insufficient data
Precision	No data (Est. ±10%)	Max. dev. from mean - 4.5% Avg. dev. from mean - 1.5%	No data
Operation Mode	Continuous	Continuous	Intermittent (Anal. filter)
Sampling Time	Approx. 1 minute (simultaneous w/analysis time)	Instantaneous	24 hours
Analysis Time	Approx. 1 minute (simultaneous w/sampling time)	Instantaneous	5 minutes
Total Cycle Time	Approx. 1 minute	Instantaneous	Approx. 24 hours
Calibration Technique	Comparison of chemical analysis for TEL in air	Air doped with TEL	Filters containing standard samples
Sample Form	Vapor or particulate	Vapor; fume; possibly particulate	Particulate on filter
Interferences	None reported	Possibly copper, halogen organics	As; possibly Br
Unit Output	mg/ft³	Mass or mass/vol.	μg
Special Equip.	None	Rf heated carbon	Vacuum or helium purge
Multi-element Application	Yes	Could be modified for individual volatile elements, e.g., Hg	Atomic number >11
Safety Hazard	High voltage electrical discharge	Moderate to high temperture; rf radiation	X-rays; moderate to high electrical voltages
Problem Areas	Particle size	Depletion of carbon in oxidizing atm.; particle size; residence times in decomposition chamber	Matrix; particle size interferences
Routine Maintenance	Replace electrodes	Replace carbon	Leak check sample chamber regularly or replace He cyl.
Volume Flow Rate	1 ft³/min.	1.2 liters/min.	--
Est. Instrument Cost	$10,000 - $20,000	$10,000 - $20,000	$10,000 - $30,000
Est. Instrument Size	4' x 2' x 6'	4' x 2' x 6'	4' x 4' x 6'

Considerable difficulty can be experienced in attempting arsenic analyses in high lead matrices by x-ray emission (fluorescence). Not only does the high absorption characteristic of the matrix cause problems, but direct spectral interference of Pb L_{α_1} radiation occurs with As K_{α_1}.

When using neutron activation analysis, particularly as a nondestructive technique, instrumentation having high resolution capability [Ge(Li) semiconductor detector] is necessary to minimize a variety of interferences in measuring arsenic and antimony in stack emission particulate.

The use of an arsine generation step aids in concentrating arsenic for atomic absorption spectrophotometry, colorimetry, and potentially flame-, rf- or microwave-excitation of emission spectra, but the total analysis time requiring collection of sample, digestion to yield trivalent arsenic, and generation of arsine is too long for short-term, intermittent measurements.

Although a long path absorption tube improves the sensitivity of the atomic absorption method for arsenic, considerable interferences (formation of arsenides, oxides) can occur, resulting in low arsenic measurements. High flame or non-flame temperatures are needed.

Considerable development work is needed to attain continuous monitoring of arsenic and antimony from stack emissions. There is no method currently available that meets the requirements for continuous monitoring of arsenic and antimony from stationary emission sources. Removal of arsenic and antimony and their compounds from the stack gases by a combination of filtration and collection in impingers followed by chemical spectrophotometric, or atom absorption spectrophotometric methods is currently the only practical approach. Some consideration should be given to determining the feasibility of using continuous arc excited emission spectrographic techniques for direct measurements for As and Sb on work environment or stack emission sources.

3.5 Summary - Analytical Technology for Continuous Monitoring of Barium, Boron, Chromium, Copper, Manganese, Nickel and Vanadium

At this time, there is no continuous monitoring system for stationary source emissions which measures B, Ba, Cr, Cu, Mn, Ni, and V as individual elements or in a multi-element functional model. Most laboratory techniques to date have been applied to integrated samples of particulate collected on filter paper from ambient air.

High sensitivities and the attendant low detection limits of the absorption and emission spectroscopic techniques make these

Table V-A

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR ARSENIC AND ANTIMONY
(Based on Literature Review)

Evaluation Parameter	Atomic Absorption Spectrophotometry			
	Arsenic			Antimony
	Conventional A.A.	A.A. w/Arsine Gen.	Absorption Tube	Conventional A.A.
Specificity	Yes	Yes	Yes	Yes
Detection Limit	1 ppm in H_2O (0.02 $\mu g/m^3$ with 2000 m^3 air sample)	0.02 μg	0.006 μg/ml	1 μg/ml
Range	Linear up to 50 μg/ml	-	-	Linear up to 40 μg/ml
Accuracy	No data	No data	No data	No data
Precision	Est. ~2%	Est. ~2%	Est. ~2%	Est. ~2%
Operation Mode	Intermittent	Intermittent	Intermittent	Intermittent
Sampling Time	Up to 24 hours	Up to 24 hours	Up to 24 hours	Up to 24 hours
Analysis Time	Depends on collection method and extraction (10 min. to 2 hrs)	10 min. to 2 hrs	10 min. to 2 hrs	Depends on collection, digestion methods; 10 min. to 2 hrs
Total Cycle Time	Approx. 24 hrs	Approx. 24 hrs	Approx. 24 hrs	Approx. 24 hrs
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Known aqueous standard solutions	Known aqueous standard solutions
Sample Form	Aqueous solutions of dissolved particulate	Arsine gas produced from particulate or fume	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate
Interferences	Flame background; flame noise; Mg, Ca, Al, Ni, Co, Mn arsenides; Fe	O_2, chromate, molybdate, metavanadate, nitrates, chlorates, Cu, Sb, H_2S	Same as Conventional A.A. but background less	Possibly Cu and Pb
Unit Output	μg/ml	μg	μg/ml	μg/ml
Special Equip.	-	Arsine generator	Heated 91 cm Vycor cell	-
Multi-Element Application	Depends on choice of lamp and flame	Possibly Sb with generator	Same as Conventional A.A.	Depends on choice of lamp and flame
Safety Hazard	Open flame	Open flame; toxic arsine gas	Flame	Open flame
Problem Areas	See Interferences above	See Interferences above; valence state As must be trivalent	See Interferences above; deposition of A_2O_3 in tube	Possibly Cu and Pb interferences
Routine Maintenance	Replace fuels	Replace fuels; change Zn and H_2SO_4 in generator	Replace fuels; clean deposit from tube	Replace fuels
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	\$5,000-\$10,000	\$5,000-\$10,000	\$7,000-\$ 5,000	\$5,000-\$10,000
Est. Instrument Size	4' x 2' x 6'	4' x 2' x 8'	4' x 2' x 9'	4' x 2' x 6'

Table V-B

Evaluation Parameter	Emission Spectroscopy				X-ray Emission (Fluorescence) Spectroscopy	
	Arsenic		Antimony			
	Flame Excitation	Rf Plasma	Flame Excitation	Rf Plasma	Arsenic	Antimony
Specificity	Yes	Yes	Yes	Yes	Interferences (Pb,W)	Yes
Detection Limit	2.2 µg/ml	0.1 µg/ml	1.0 µg/ml	0.2 µg/ml	1-10 µg (Depends on matrix)	2 µg (Depends on matrix)
Range	No data	No data	No data	No data	Dependent on matrix	Dependent on matrix
Accuracy	No data	No data	No data	No data	No data	No data
Precision	No data	No data	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent	Intermittent	Intermittent (Anal. filter)	Intermittent (Anal. filter)
Sampling Time	Up to 24 hrs	Up to 24 hrs	Up to 24 hrs	Up to 24 hrs	Up to 24 hrs	Up to 24 hrs
Analysis Time	10 min-24 hr depending on sample prep.	10 min-24 hr depending on sample prep.	10 min-24 hr depending on sample prep.	10 min-24 hr depending on sample prep.	∿5 min	∿5 min
Total Cycle Time	Approx. 24 hrs	Approx. 24 hrs	Approx. 24 hrs	Approx 24 hrs	Approx. 24 hrs	Approx. 24 hrs
Calibration Technique	Standard solutions	Standard solutions	Standard solutions	Standard solutions	Filters containing deposits of known concentration	Filters containing deposits of known concentration
Sample Form	Aq. solution of dissolved particulate or fume	Aq. solution of dissolved particulate or fume	Aq. solution of dissolved particulate or fume	Aq. solution of dissolved particulate or fume	Particulate on filter	Particulate on filter
Interferences	Zn, Cd, Possibly Sn & Ni	Cd	As	None reported	Pb and W, Matrix absorption	Matrix absorption
Unit Output	µg/ml	µg/ml	µg/ml	µg/ml	µg	µg
Special Equip.	-	-	-	-	Vacuum or helium purge	Vacuum or helium purge
Multi-Element	Depends on excitation potential	Yes	Depends on excitation potential	Yes	Atomic number >11	Atomic number >11
Safety Hazard	Flame	Flame and rf radiation	Flame	Flame and rf radiation	X-rays; moderate to high electrical voltages	X-rays; moderate to high electrical voltages
Problem Areas	See Interferences above; selection of anal. line & slit width; possibly formation of arsenides in flame	Cd	None reported	None reported	Matrix (particularly lead); particle size effects	Matrix (particularly lead alloys); particle size effects
Routine Maintenance	Replace fuels	Replace carrier gas	Replace fuels	Replace carrier gas	Leak check sample chamber regularly or replace He cylinder	Leak check sample chamber regularly or replace He cylinder
Volume Flow Rate	-	-	-	-	-	-
Est. Instrument Cost*	$5,000-$15,000	$5,000-$17,500	$5,000-$15,000	$5,000-$17,500	$10,000-$30,000	$10,000-$30,000
Est. Instrument Size	4' x 2' x 6'	4' x 2' x 8'	4' x 2' x 6'	4' x 2' x 8'	4' x 4' x 6'	4' x 4' x 6'

*Cost depends on resolution, detection limit, and sample time required, which in turn depends on the sample matrix.

techniques most attractive for continuous or short-term, intermittent monitors. By maintaining the element sought in the stack gas and by introducing the stack gas as part of the oxidant or fuel in the flame or high energy discharge of the excitation source of the spectrometer, a continuous monitoring system is possible. With B, Ba, Cr, Cu, Mn, Ni, and V, the major problems with using the absorption or emission spectroscopic techniques are the inter-element or compound formation effects.

With atomic absorption spectrophotometry, the inter-element or compound formation effects are minimized or eliminated by using a nitrous oxide-acetylene flame. The best results are obtained with a sheath gas (inert gas, e.g., nitrogen) to exclude oxygen from the flame. Obviously, in ambient air or stack emissions, elimination of the oxygen is extremely difficult. One possible way is to pass the stack gas or air over hot carbon to produce carbon monoxide.

The use of an inert gas plasma as an atomization source for atomic absorption spectrophotometry will also minimize inter-element effects if a reducing atmosphere is maintained in the plasma. The reducing atmosphere can be maintained by introducing hydrogen gas. An additional problem related to the use of a plasma to provide the atomization for atomic absorption measurements is the possibility of overexciting the element sought to emission, rather than to the necessary ground energy state. As a result, the population of ground state atoms may be too low to attain maximum sensitivity. Generally, the selection of the "viewing zone" of the plasma must be optimized depending on the element to be measured.

Although flame photometry can be used for measuring Ba and a number of other elements, inter-element and compound formation effects are also a problem. These effects can be minimized by using a nitrous oxide-acetylene flame.

Some inter-element effects are observed in arc- or spark-emission spectroscopy, but these can be eliminated by using high energy excitation, e.g., a radio-frequency plasma. Continuous monitoring systems for Be, Hg, and Pb, based on emission spectroscopy, have been developed using arc- or spark-excitation. Similar approaches with either an arc-or-spark excitation or a radio-frequency plasma can be applied to other elements. With a radio-frequency induced plasma, emission spectrographic analyses for B, Ba, Cr, Cu, Mn, Ni, and V without inter-element effects and on a continuous operational mode are possible. Repeated scanning of plasma induced emission lines of chromium and manganese show high stability as indicated by relative standard deviations of intensities of 1.9% and 1.7%, respectively, when the sample is introduced continuously as an aqueous solution.

X-ray emission (fluorescence) spectrometry is not applicable for measuring boron emissions. With a high resolution semiconductor detector, x-ray emission techniques with conventional x-ray target tubes and with radioisotope sources can be used on an intermittent basis to determine Ba, Cr, Cu, Mn, Ni, and V in particulate collected on filters. Care must be taken to measure thin film deposits so as to minimize matrix effects. Also, the background of secondary emission of x-rays from the filter media can be a major interference.

Radio-isotope sources for x-ray emission measurements provide a high degree of portability and simplicity of ancillary equipment. When applied to monitoring particulate collected on filters, good accuracy and repeatability of measurements are obtained (see Appendix VI, Section 3.4, Rhodes ref. 88,89). The major limitations in applying the x-ray techniques are the time to collect sufficient particulate on the filter and the potential loss of volatile emissions containing the element sought.

Nondestructive neutron activation analysis can be performed on particulate for certain elements, but not all. The major problem is the interference from radioactive isotopes of other elements. Lengthy cooling times ranging from several hours to several months are necessary to obtain sufficient sensitivity for some elements, particularly Cr and Ni. Manganese and vanadium can be measured immediately. Depending on the detection level required, copper can be measured immediately or, if a lower detection level is necessary, after 20-30 hr decay time.

By using high intensity reactor pulsing techniques, boron can be determined by nondestructive neutron activation analysis techniques, but not by conventional steady-state thermal neutron irradiation.

With fast neutrons from an isotopic source, much shorter irradiating and cooling times are possible. There is some sacrifice of sensitivity, but the technique provides for detecting Ba, Cr, Cu, Mn, and V in approximately 30 minutes total time. Measurement of Ni can be accomplished in approximately 2 hours.

Continuous, on-stream (aqueous solutions), neutron activation analyses of V and Mn have been performed with isotopic sources at the $\leq$100 ppm level in 5-10 minute cycles.

The chemiluminescent reaction of $Ni(CO)_4$ with ozone in presence of carbon monoxide deserves consideration as a possible system for continuous monitoring of $Ni(CO)_4$ emissions. Possible applications including monitoring: (a) effluent from the Mond process of refining nickel, (b) formation of $Ni(CO)_4$ when CO in effluent emissions passes over or through nickel products or alloys, and (c) losses of nickel metal particulate from filter media in particulate sampling systems.

In special cases, continuous colorimetric measures are possible for certain boranes. However, the application of the techniques must be made with care to ensure absence of interferences.

Measuring boron indirectly with mass spectrometry by determining the number of helium atoms generated in the $^{10}B(n,\alpha)$ reaction should be further evaluated.

Table VI

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR BARIUM
(Based on Literature Review)

Evaluation Parameter	Atomic Absorption Spectrophotometry	Emission Spectroscopy		X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
		Flame	RF Plasma		
Specificity	Yes	Yes	Yes	Yes	Yes
Detection Limit	0.02 μg/m^3[a]	0.0035 μg/ml	0.0001 μg/ml		0.02 μg
Range	-	-	-	No data	No data
Accuracy	No data	No data	No data	No data	No data
Precision	No data	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent	Intermittent (Anal. Filters)	Intermittent (Anal. Filters)
Sampling Time	24 hrs	No data	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	→	→	10-30 min	30 min
Total Cycle Time	~24 hrs	-	-	24-25 hrs	24-25 hrs
Calibration Technique	Known aqueous standard solutions	→	→	Known samples on filter	Known samples
Sample Form	Aqueous solutions of dissolved particulate	→	→	Particulate on filter	Particulate on filter
Interferences	Cationic & anionic	Cationic & anionic	None reported	Matrix absorption; particle size	Background from filters; matrix background?
Unit Output	μg/m^3	μg/ml	μg/ml	μg	μg
Special Equip.	Nitrous oxide-acetylene flame	Nitrous oxide-acetylene flame	Argon	Vacuum or helium purge	Neutron reactor or isotope source
Multi-element Application	Depends on choice of lamp and flame	Yes, for selected elements	Yes	Atomic number >11	Yes, but certain elements may require chemical separation
Safety Hazard	Open flame	Open flame	Flame; high voltage; RF radiation	X-rays; moderate to high electrical voltages	Radiation
Problem Areas	Cationic & anionic interferences	Cationic & anionic interferences	None reported	Matrix, interelement, and particle size effects; background from filters, resolution	Background from filters; some matrix background
Routine Maintenance	Replace fuels	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber, if used	-
Volume Flow Rate	-	-	-	-	-
Est. Instrument Cost	\$5,000-10,000	\$5,000-10,000	\$5,000-17,500	\$10,000-30,000	>\$100,000[b]
Est. Instrument Size	4' x 2' x 6'	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor[c]

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[a] 2000 m^3 sample

[b] Isotopic source may reduce price

[c] Isotopic source may reduce size and weight

Table VII

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR BORON
(Based on Literature Review)

Evaluation Parameter	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes
Detection Limit	3-6 μg/ml	0.03 μg/ml	1.1 μg
Range	Linear up to 200 μg/ml	-	No data
Accuracy	No data	No data	No data
Precision	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent
Sampling Time	∿24 hrs	No data	24 hrs
Analysis Time	Depends on collection method and extraction	Depends on collection method and extraction	30 min
Total Cycle Time	∿24 hrs	∿24 hrs	∿24 hrs
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Known standard samples
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate
Interferences	Matrix, oxide formation	None reported	Some matrix effects
Unit Output	μg/ml	μg/ml	μg
Special Equip.	Nitrous oxide-acetylene flame	Argon	Requires pulsed neutron flux
Multi-element Application	Depends on choice of lamp and flame	Yes	B, Be, Li, O, F, Mg, and Pb in pulsed mode
Safety Hazard	Open flame	Flame; high voltage; RF radiation	Radiation
Problem Areas	Refractory nature of boron; needs high temperature flame	None reported	Matrix effects
Routine Maintenance	Replace fuels	Replace Argon	-
Volume Flow Rate	-	-	-
Est. Instrument Cost	$5,000-10,000	$5,000-17,500	>$100,000[a]
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	Massive reactor[b]

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[a] & [b] Isotopic source may reduce cost and size.

Table VIII

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR CHROMIUM
(Based on Literature Review)

Evaluation Parameters	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes (requires proper resolution)	Yes
Detection Limit	0.002 $\mu g/m^3$	0.001 μg/ml	0.053 $\mu g/m^3$	0.02 μg
Range	-	-	No data	-
Accuracy	No data	No data	No data	No data
Precision	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent (Anal. filters)	Intermittent (Anal. filters)
Sampling Time	24 hrs	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	Depends on collection method and extraction (10 min to 2 hrs)	Approximately 1 hour	Requires 20-30 day decay time or chemical separation
Total Cycle Time	~24 hrs	-	~24 hrs	-
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Standard samples of particulate on filters	Standard samples of particulate on filters
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate on filters	Particulate on filters
Interferences	Interelement effects	None reported	Filter background; matrix elements; inter-element effects	Matrix elements
Unit Output	$\mu g/m^3$	μg/ml	μg	μg
Special Equip.	Should use nitrous oxide-acetylene flame	Argon	Vacuum or helium purge; semiconductor detector	-
Multi-element Application	Depends on choice of lamp and flame	Yes	Atomic number >11	Yes
Safety Hazard	Open flame	Flame; high voltage; RF radiation	X-ray; moderate to high electrical voltages	Radiation
Problem Areas	Interelement effects	None reported	Matrix; interelement and particle size effects; background from filters; resolution	Matrix elements which require chemical separation or lengthy decay times
Routine Maintenance	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber	-
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	$5,000-10,000	$5,000-17,500	$10,000-30,000	>$100,000
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor

Table IX

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR COPPER
(Based on Literature Review)

Evaluation Parameters	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes, with proper resolution	Yes
Detection Limit	0.001 $\mu g/m^3$	Insufficient data	0.011 $\mu g/m^3$	0.1 μg
Range	-	-	No data	-
Accuracy	No data	No data	No data	No data
Precision	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent (Anal. filters)	Intermittent (Anal. filters)
Sampling Time	24 hrs	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	Depends on collection method and extraction (10 min to 2 hrs)	Approximately 1 hour	Requires 3 min decay time
Total Cycle Time	~24 hrs	-	~24 hrs	-
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Standard samples of particulate on filters	Standard samples of particulate on filters
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate on filters	Particulate on filters
Interferences	Interelement effects	None reported	Filter background; matrix elements; inter-element effects	Matrix elements
Unit Output	$\mu g/m^3$	$\mu g/ml$	μg	μg
Special Equip.	Should use nitrous oxide-acetylene flame	Argon	Vacuum or helium purge; semiconductor detector	-
Multi-element Application	Depends on choice of lamp and flame	Yes	Atomic number >11	Yes
Safety Hazard	Open flame	Flame; high voltage; RF radiation	X-ray; moderate to high electrical voltages	Radiation
Problem Areas	Interelement effects	None reported	Matrix; interelement and particle size effects; background from filters; resolution	Requires 3 min decay time
Routine Maintenance	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber	-
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	\$5,000-10,000	\$5,000-17,500	\$10,000-30,000	>\$100,000
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor

Table X

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR MANGANESE
(Based on Literature Review)

Evaluation Parameters	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes, with proper resolution	Yes
Detection Limit	0.001 $\mu g/m^3$	Insufficient data	0.027 $\mu g/m^3$	0.003 μg
Range	-	-	No data	-
Accuracy	No data	No data	No data	No data
Precision	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent (Anal. filters)	Intermittent (Anal. filters)
Sampling Time	24 hrs	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	Depends on collection method and extraction (10 min to 2 hrs)	Approximately 1 hour	Requires 15 min decay time
Total Cycle Time	~24 hrs	-	~24 hrs	-
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Standard samples of particulate on filters	Standard samples of particulate on filters
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate on filters	Particulate on filters
Interferences	Interelement effects	None reported	Filter background; matrix elements; inter-element effects	Matrix elements
Unit Output	$\mu g/m^3$	$\mu g/ml$	μg	μg
Special Equip.	Should use nitrous oxide-acetylene flame	Argon	Vacuum or helium purge; semiconductor detector	-
Multi-element Application	Depends on choice of lamp and flame	Yes	Atomic number >11	Yes
Safety Hazard	Open flame	Flame; high voltage; RF radiation	X-ray; moderate to high electrical voltages	Radiation
Problem Areas	Interelement effects	None reported	Matrix; interelement and particle size effects; background from filters; resolution	Requires 15 min decay time
Routine Maintenance	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber	-
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	\$5,000-10,000	\$5,000-17,500	\$10,000-30,000	>\$100,000
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor

Table XI

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR NICKEL
(Based on Literature Review)

Evaluation Parameters	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes, with proper resolution	Yes
Detection Limit	0.004 μg/m³	0.006 μg/ml	0.013 μg/m³	1.5 μg
Range	-	-	No data	-
Accuracy	No data	No data	No data	No data
Precision	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent (Anal. filters)	Intermittent (Anal. filters)
Sampling Time	24 hrs	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	Depends on collection method and extraction (10 min to 2 hrs)	Approximately 1 hour	Requires chemical separation or 20-30 day decay time
Total Cycle Time	~24 hrs	-	~24 hrs	-
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Standard samples of particulate on filters	Standard samples of particulate on filters
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate on filters	Particulate on filters
Interferences	Interelement effects	None reported	Filter background; matrix elements; inter-element effects	Matrix elements
Unit Output	μg/m³	μg/ml	μg	μg
Special Equip.	Should use nitrous oxide-acetylene flame	Argon	Vacuum or helium purge; semiconductor detector	-
Multi-element Application	Depends on choice of lamp and flame	Yes	Atomic number >11	Yes
Safety Hazard	Open flame	Flame; high voltage; RF radiation	X-ray; moderate to high electrical voltages	Radiation
Problem Areas	Interelement effects	None reported	Matrix; interelement and particle size effects; background from filters; resolution	Requires chemical separation or 20-30 day decay time
Routine Maintenance	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber	-
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	$5,000-10,000	$5,000-17,500	$10,000-30,000	>$100,000
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor

Table XII

SUMMARY OF EVALUATION PARAMETERS FOR MONITORING SYSTEMS FOR VANADIUM
(Based on Literature Review)

Evaluation Parameters	Atomic Absorption Spectrophotometry	RF Plasma Emission Spectroscopy	X-ray Emission (Fluorescence) Spectroscopy	Neutron Activation Analysis
Specificity	Yes	Yes	Yes, with proper resolution	Yes
Detection Limit	0.01 $\mu g/m^3$	0.006 $\mu g/ml$	0.007 $\mu g/m^3$	0.001 μg
Range	-	-	No data	-
Accuracy	No data	No data	No data	No data
Precision	No data	No data	No data	No data
Operation Mode	Intermittent	Intermittent	Intermittent (Anal. filters)	Intermittent (Anal. filters)
Sampling Time	24 hrs	No data	24 hrs	24 hrs
Analysis Time	Depends on collection method and extraction (10 min to 2 hrs)	Depends on collection method and extraction (10 min to 2 hrs)	Approximately 1 hour	3 min decay time
Total Cycle Time	∿24 hrs	-	∿24 hrs	-
Calibration Technique	Known aqueous standard solutions	Known aqueous standard solutions	Standard samples of particulate on filters	Standard samples of particulate on filters
Sample Form	Aqueous solutions of dissolved particulate	Aqueous solutions of dissolved particulate	Particulate on filters	Particulate on filters
Interferences	Interelement effects	None reported	Filter background; matrix elements; inter-element effects	Matrix elements
Unit Output	$\mu g/m^3$	$\mu g/ml$	μg	μg
Special Equip.	Should use nitrous oxide-acetylene flame	Argon	Vacuum or helium purge; semiconductor detector	-
Multi-element Application	Depends on choice of lamp and flame	Yes	Atomic number >11	Yes
Safety Hazard	Open flame	Flame; high voltage; RF radiation	X-ray; moderate to high electrical voltages	Radiation
Problem Areas	Interelement effects	None reported	Matrix; interelement and particle size effects; background from filters; resolution	3 min decay time
Routine Maintenance	Replace fuels	Replace Argon	Maintain vacuum or helium purge to sample chamber	-
Volume Flow Rate	-	-	-	-
Est. Instrument Cost	$5,000-10,000	$5,000-17,500	$10,000-30,000	>$100,000
Est. Instrument Size	4' x 2' x 6'	4' x 4' x 8'	4' x 4' x 6'	Massive reactor

4. PRELIMINARY FIELD STUDIES

An evaluation of the published information available for the four stationary sources - power plant, incinerator, ore refineries, and machining operation - identified as being major sources of beryllium and cadmium revealed the lack of specific process information which defines the physical and chemical properties of the emissions. Process data was needed to establish the sensitivity and resolution requirements of the monitor, its concentration span, the potential sources of interference (chemical and physical) that it must cope with, and the requirements of sampling and delivery equipment to ensure that a representative sample is presented to the analyzer.

A preliminary field test study at three field test sites - power plant, incinerator, and machining operation - was devised to establish the following information:

Rate of emission of Be and Cd, weight/volume of effluent.

Overall composition of emission, including potential interferences (gases, aerosols, and other metals).

Representative particle size distribution of particulate emitted.

Distribution of Be and Cd within this size distribution.

4.1 Preliminary Sampling Study - Power Station

Samples were collected from the power station site at a 15-ft square duct after the electrostatic precipitator and after the I.D. Fan. The sample was taken with a Brink® Model BMS-11 Cascade Impactor through a 3-in. diameter port. The objective of this effort was to determine the particle size distribution of the fly ash and establish the sensitivity of the sampling system to non-isokinetic sampling practices.

The Brink® Cascade Impactor contains a glass cyclone, a five stage impactor and a dust filter assembly. The cyclone removes all particles larger than 7 microns from the gas sample with the remainder of the dust collected in the impactor according to particle size; i.e., the largest particles collecting in the first stage and successively smaller particles collecting on the lower stages. Table XIII lists the particle size range collected in each stage of the impactor for the sampling conditions employed in this study.

Since the objective of this effort was to determine the sensitivity of the Be/Cd sampling system to non-isokinetic sampling, the flow rate through the nozzle of the probe was set below isokinetic velocity to favor the collection of the larger

Table XIII

BERYLLIUM AND CADMIUM CONTENT OF PARTICULATE COLLECTED FROM POWER STATION

				Analyses of Combined Runs I & II			
				Be		Cd	
Stage	Particle Size Range (microns)	Particulate Collected (mg) (Runs I & II)		Conc. as Particulate in Flue Gas (μg/m³)	Conc. in Particulate (ppm)	Conc. as Particulate in Flue Gas (μg/m³)	Conc. in Particulate (ppm)
Cyclone	>7.0	0.00	0.00	-	-	-	-
First	1.9-7.0	6.29	7.605	20.5	118	0.53	3.4
Second	1.1-1.9	2.735	2.08	7.7	127	0.50	9.5
Third	0.74-1.1	0.88	0.535	1.6	88	N.D.	N.D.
Fourth	0.36-0.74	0.44	0.205	0.47	59	~0.11	14
Fifth	0.24-0.36	0.10	0.05	~0.10	~53	N.D.	N.D.
Filter	0.2-0.24	0.135	0.105	-	-	-	-
Total		10.58	10.58	30.4		1.14	

Footnotes:

(1) Particulate size distribution obtained with the Brinks Cascade Impactor.

(2) Analyses performed by Atomic Absorption Spectrophotometry-Carbon Rod Assembly.

(3) Sample taken from power station flue gas after electrostatic precipitator.

(4) N.D. - Not detectable above blank.

particle sizes. Should the mass median particle size obtained under these sampling conditions be below 5 microns, it would be safe to assume that a reasonably representative dust sample could be obtained even under non-isokinetic conditions. Table XIII gives the weight of dust collected in each stage for two different dust samples.

The particle size distributions are shown graphically in Figure 1. For both samples, more than 80 wt-% of the collected particles had diameters below 5 microns. Since these samples were obtained under sub-isokinetic conditions, the particle size distribution is skewed towards the larger particle sizes. An isokinetic sample might therefore give an even higher percentage of particles below 5 microns. With this information it is safe to assume that a reasonably good sample from power plant flue gas can be obtained without isokinetic sampling.

The particulate collected in the various stages of the Brink Cascade Impactor was digested with an acid solution (see Preliminary EPA Method 11. Determination of Beryllium from Stationary Sources) and analyzed for beryllium and cadmium by non-flame atomic absorption spectrophotometry. The atomic absorption measurements were made with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a Varian Techtron Model 61 Carbon Rod Atomizer.

The analyses for the power plant are reported in Table XIII. The results for the power plant were obtained by combining the collected fractions for two flue gas samplings.

Based on two 20-minute collections at a flow rate of 2 liters/min., the analyses indicate concentrations in the flue gas of approximately 30 μg Be/m^3 and 1.2 μg Cd/m^3 in particles between 0.24 micron and 7.0 microns. Analysis of fly ash deposited in the flues shows a concentration of 89 ppm of Be in the ash. The beryllium content appears to be lower in the smaller particles than in the larger particles, whereas the limited data suggest the opposite for cadmium.

The semi-quantitative emission spectrographic analysis of particulate (power plant) from the first stage of Brink Cascade Impactor is shown in Table XIV.

4.2 Preliminary Sampling Study - Municipal Solid Waste Incinerator

A particulate sample was collected from a port in the exhaust stack of a municipal incinerator after the caustic scrubber by using a Brink® Model BMS-11 Cascade Impactor described in Section 4.1 of this report.

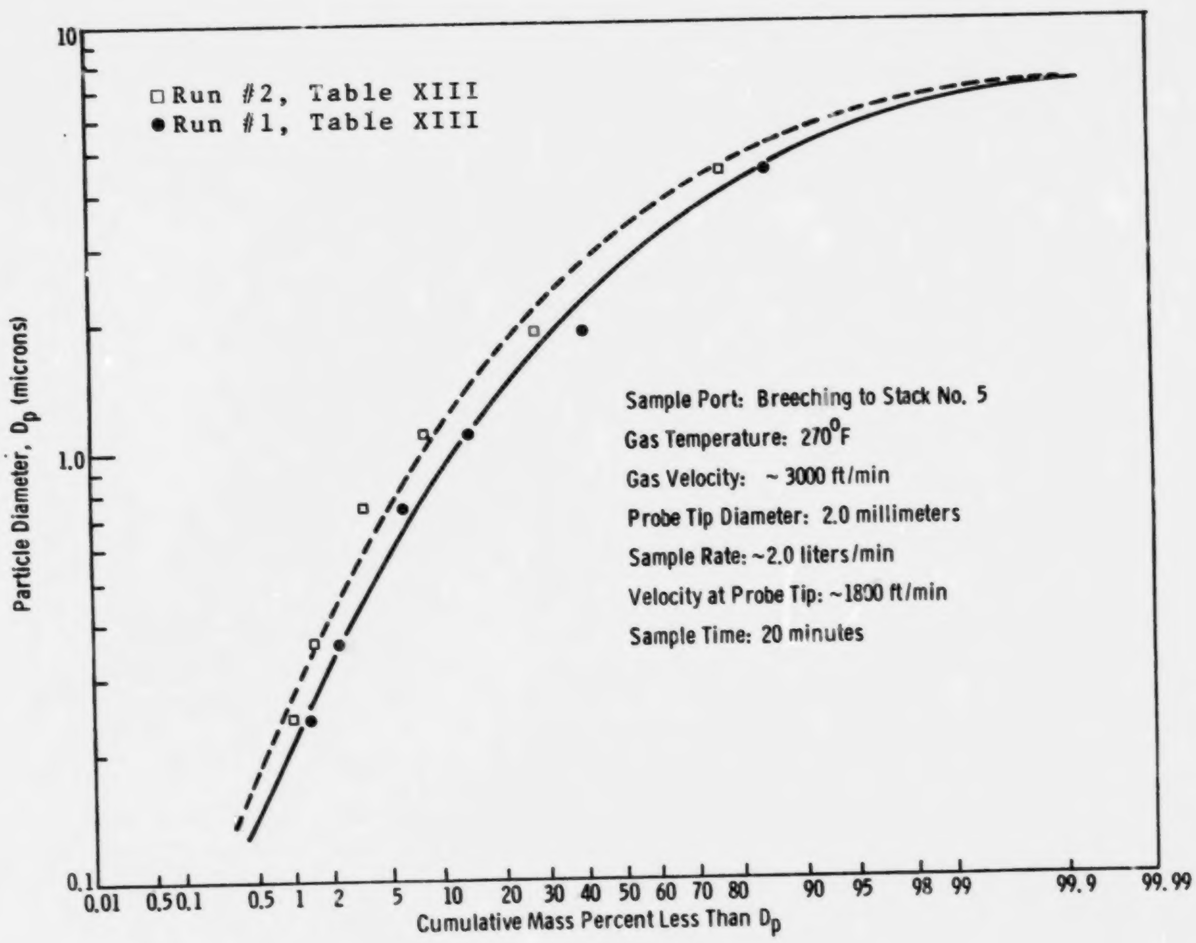

Figure 1. Fly Ash Particle Size Distribution From Power Plant Test Site (February 1972).

Table XIV

SEMI-QUANTITATIVE (±20%) EMISSION SPECTROGRAPHIC ANALYSIS OF PARTICULATE FROM 1st STAGE OF BRINK® CASCADE IMPACTOR

Al - Major Constituent

Si - Major Constituent

Fe - Minor Constituent

Mg - 0.7%

Ca - 0.6%

Ti - 0.3%

Na - 0.3%

Cu - 0.05%

Mn - 0.03%

Ni - 0.02%

Zr - 0.02%

V - 0.02%

Be - Not Detected; if present <0.01% (<100 ppm)

Cd - Not Detected; if present <0.05% (<500 ppm)

The first attempt (Run I) to sample the incinerator by "conventional techniques," i.e., by withdrawing a sample from the stack through a heated line, proved to be inadequate. The temperature of the delivery line could not be controlled within the narrow temperature range required to prevent condensation of water vapor or evaporation of entrained water. In the first sampling test, a considerable quantity of water was collected in the cyclone and none in the impactor.

To eliminate the problems associated with transporting the sample to the impactor, the sampling procedure was changed as follows for Run II.

1. The impactor was removed from the sample case.
2. The sampling nozzle was fitted directly into the impactor inlet.
3. Thirty-foot lengths of rubber tubing were connected to the inlet and out pressure taps and vacuum outlet.
4. The impactor was lowered into the stack by means of a suitable length of rope.

The impactor was lowered into the stack about two feet from the stack wall by means of an extension rod. To prevent condensation of liquid within the cold impactor, it was held in the stack for two minutes prior to sampling.

The gas flow rate was adjusted to 3.0 liters/minute and maintained at this rate for 10.0 minutes. Thus, a total of 30 liters (0.03 m^3) was sampled.

The particulate collected in the various stages of the Brink Cascade Impactor was digested with an acid solution (see Preliminary EPA Method 11. Determination of Beryllium from Stationary Sources) and analyzed for beryllium and cadmium by non-flame atomic absorption spectrophotometry. The atomic absorption measurements were made with a Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a Varian Techtron Model 61 Carbon Rod Atomizer.

During the collection of aerosol from the incinerator (Run II), liquid condensate was deposited in each impact compartment of the Brink Cascade Impactor and no weights of individual fractions could be obtained. However, by allowing the moisture to evaporate at room temperature and dissolving the residue in known volumes of high purity acid, estimates of the distribution of aerosol and the concentration of Be and Cd can be made. These results are reported in Table XV.

Table XV

BERYLLIUM AND CADMIUM CONTENT OF PARTICULATE AND AEROSOL COLLECTION FROM MUNICIPAL SOLID-WASTE INCINERATOR

Particle Size (microns)	Concentration of Element Collected as Particulate or Aerosol ($\mu g/m^3$)			
	Run I		Run II	
	Be	Cd	Be	Cd
7.0 (Cyclone)	1.9	46	N.C.	N.C.
1.9-7.0	N.D.	0.097	0.083	0.016
1.9-1.9	N.D.	0.064	0.10	0.31
0.74-1.1	N.D.	0.033	0.13	12
0.36-0.74	N.D.	N.D.	0.073	7.3
0.24-0.36	N.D.	0.093	0.033	17
Total	1.9	46	0.42	37

Footnotes:

(1) Particulate size distribution obtained with the Brinks Cascade Impactor.

(2) Analyses performed by Atomic Absorption Spectrophotometry-Carbon Rod Assembly.

(3) N.D. - Not detected

(4) N.C. - Not collected

(5) Approximately 2 ml of water was obtained as condensate in the cyclone.

Two collections of aerosols were made. Run I was performed with little control of inlet heat to the impactor and as a consequence the water aerosol deposited principally as condensate in the first stage (cyclone). Better control of inlet heat on the impactor in Run II resulted in aerosol deposition through the train. When condensation occurred (Run I), no beryllium was detected in the impactor stages which would isolate particulate in the 0.24 micron to 7.0 micron range; however, very small quantities of cadmium were detected in a relatively uniform distribution in 4 of the 5 stages in the same particle size range.

When condensation was minimized (Run II), concentrations of approximately 0.4 to 2 μg Be/m³ and 40 μg Cd/m³ were collected in the particle size range of 0.24 micron to 7.0 microns. The distribution of beryllium appears to be approximately the same in the four stages through the particle size range of 0.36 micron to 7.0 microns, but slightly lower in the range of 0.24-0.36 micron. The distribution of cadmium in the various stages of the cascade impactor is markedly different from that observed for beryllium; cadmium concentrations are greater on the stages that isolate the smaller particles 0.24 micron to 1.1 microns, than on the stages retaining particles of 1.1 microns to 7.0 microns.

4.3 Preliminary Field Study - Machining Operation of Beryllium Metal

Preliminary stack emission samples were taken at a machining operation which was being considered as a candidate field test site. The machining operation has three metal cutting machines which fabricate beryllium metal parts. On the day for sampling, only one of the three was operating. Visual inspection of the air leaving the plant suggested that a high volume of sample would be required to obtain a measurable quantity of particulate. The sample probe was located after the fan and two absolute filters in the dust cleaning system. Visual inspection of the dust cleaning system further suggested that the particles that pass through the second absolute filter are of a very small size. For this reason, the cascade impactor was abandoned in favor of a 0.2 micron filter.

A total of 240 cu.ft was drawn through the filter over a period of four hours (1.0 cfm). Weighing the filter paper after the sampling period revealed no apparent weight gain. The balance has a maximum accuracy of 0.05 mg. If it is assumed that 0.05 mg was deposited upon the filter, then the dust concentration would be:

$$\frac{0.05\ \text{mg}}{240\ \text{cu.ft}} \times \frac{35.2\ \text{cu.ft}}{\text{m}^3} = \frac{0.007\ \text{mg}}{\text{m}^3}$$

No beryllium was detected by atomic absorption spectrophotometric analysis of the filter.

5. INSTRUMENT DESIGN AND FEASIBILITY (LABORATORY) TESTING

5.1 Selection of Prototype Design

5.1.1 Direction Indicated for Experimental Plan

An evaluation of the literature data and the preliminary field studies indicated that a monitor based on continuous-flow emission spectrographic techniques was the most promising of all approaches currently available for monitoring Be and Cd from stationary source emissions. Earlier studies with arc excitation, showing a detection limit of 0.5 to 1 μg Be/m^3 at flow rates of 40 l/min, demonstrated the application of the technique for continuous monitoring of Be emission in work environment atmospheres with approximately 30-60 second sampling times. Several instruments based on the emission spectroscopic concept had been used for monitoring Be in England, France, Yugoslavia, Japan, and the United States.

In all previous applications, the emission spectrographic technique was applied to relatively clean atmospheres containing small quantities of particulate composed of principally beryllium or its compounds. The potential problems of electrode wear and of particulate depositing on electrodes of the arc system or not being completely vaporized or excited to generate optical emission spectra, indicated the desirability for an electrodeless, more energetic, discharge system. Therefore, a development program involving an electrodeless radio-frequency induced plasma was devised to develop an excitation system where the stack gases could be excited to optical emission directly or after dilution with an inert gas and where the problems of electrode wear and particulate deposition would be eliminated. The major problems anticipated for the radio-frequency induced plasma were the ability to maintain a stable plasma in an air rich gas and to detect elemental optical emission spectra which would not be affected by oxidation phenomena in the air matrix.

The program included three separate, but related, approaches to generating the optical emission spectra:

1. A commercial radio-frequency (RF) generator capable of variable frequencies output (15 to 50 MHz) and a maximum continuous power output of 2500 watts was applied to develop air and argon-air plasmas.

2. An attempt was made to develop a light-weight, portable, radiofrequency (RF) generator system based on an amateur radio transmitter and a high frequency linear amplifier which was tunable from 21 to 21.5 MHz or 28.5 to 29 MHz with a continuous power output capability of 1250 watts. The system would provide an electrodeless RF induced plasma in air or air-argon mixtures.

3. The Webb cell (see Appendix VII, Section 2.3) was obtained from the developer for use in an AC discharge (Pt electrode) system.

Initially, the discharge systems were evaluated in laboratory tests to establish feasibility. Finally, the Webb arc discharge system was evaluated in field tests at a power plant.

5.1.2 Source Sampling Considerations

A valid stationary source monitoring system must deliver a representative sample of the emission components to be monitored to the analytical detector. Appendix I of this report presents a detailed discussion of sampling system considerations.

Previous experience by the Environmental Protection Agency in sampling and collection of particulate from a beryllium machining plant using a typical EPA sampling train indicated that beryllium was uniformly distributed throughout the train. In general, little beryllium-containing particulate was obtained on the filter and a majority of the metal was found on analysis of the probe wash solution or in the impinger train. The beryllium found in the impinger train did not decrease progressively when a number of impingers were arranged in sequence. This slippage of material through the filter and the potential problems in volatilization of metals in the oxidizing and reactive gas constituents characteristic of a number of stationary sources points to selection of a monitoring system where all of the emission components are sampled and transported to an analysis stage as a combined vapor/aerosol mixture. This approach in turn is dependent upon selection of an analytical detection approach for Be/Cd which will not be adversely affected by the presence of all other components in the emissions matrix.

The preliminary field studies discussed in the previous subsection indicated that the particulate containing beryllium and cadmium from three major sources was largely in size ranges amenable to non-isokinetic sampling (e.g., $<4\mu$ diameter; see Appendix I, Section 3.0). Any industrial facility, however, which employs a wet scrubber treatment will emit a binodal particle size distribution. One maximum is associated with water droplets $>30\mu$ in diameter and the other maximum associated with particulate generally below 5μ in diameter. Since the water droplets can incorporate fine particulate containing beryllium and cadmium, an isokinetic sampler must be employed to accommodate a facility employing a wet scrubber stage.

Appendix I contains a detailed examination of the requirements for isokinetic sampling and the design of the sample transport system required to minimize wall loss of sampled aerosol by gravitational settling or diffusion. Fuchs' treatise on the mechanics of aerosols (ref. 16) was employed to conduct calculations of flow rates, transfer line diameters, etc., which would optimize transport of the sampled aerosol from the sampling probe to the analysis instrumentation. This analysis showed that aerosol loss by diffusion to the transport line walls would be negligible for any line diameter. This conclusion is in contrast to the situation when sampling of pollutant gases is desired, since these gases have diffusion coefficients several orders of magnitude larger than even submicron particulate.

The major considerations, therefore, for proper sampling of particulate matter and interface with the analyzer are to ensure isokinetic sampling conditions and to design the sample transport lines in a manner to minimize settling of particulate under the influence of gravity. Based on these considerations, a sampling system was designed which included isokinetic sampling of a primary stream at flow rates of about 2 cu.ft./min. followed by secondary sampling of this primary stream to isolate a constant flow sample for delivery to the analytical instrumentation. The sampling system was designed to employ an isokinetic sampling probe system. The secondary sampling of this stream was designed and packaged in a Be/Cd sampling compartment where the gas transport system is interfaced with the rf-induced emission spectroscopy technique. A schematic of the Be/Cd sample compartment is shown in Figure 2.

Later, field testing of the AC discharge arc emission detection approach was conducted at a power plant employing a sampling facility used earlier on Contract EHSD 71-30. This field sampling facility is described in detail in Appendix I.

5.2 Radio-Frequency Excited Optical Emission Spectroscopy

5.2.1 Instrumentation

Two types of excitation sources (a) Lepel generator and (b) Drake radio transmitter were used to generate radio-frequency (RF) induced plasmas. The Lepel generator, weighing approximately 270 pounds and requiring a 15-gallon heat exchanger is not portable, but is transportable and costs $3200. The Drake radio transmitter system weighs less than 100 pounds, requires minimal water cooling (1/2 gal/min) and power, and costs $2200.

Both systems provide a tunable frequency generator capable of producing a radio-frequency of 30 MHz. This frequency has been used successfully to initiate and sustain radio-frequency induced plasmas in a variety of spectroscopic studies (ref. 8,9,10).

5.2.1.1 Lepel Radio-Frequency Generator System

The Lepel generator is a high-frequency induction heating unit (Lepel Model T-2.5-1-MC2-BW Type T-252-53, Lepel High Frequency Laboratories, Inc., 59-21 Queens Midtown Expressway,

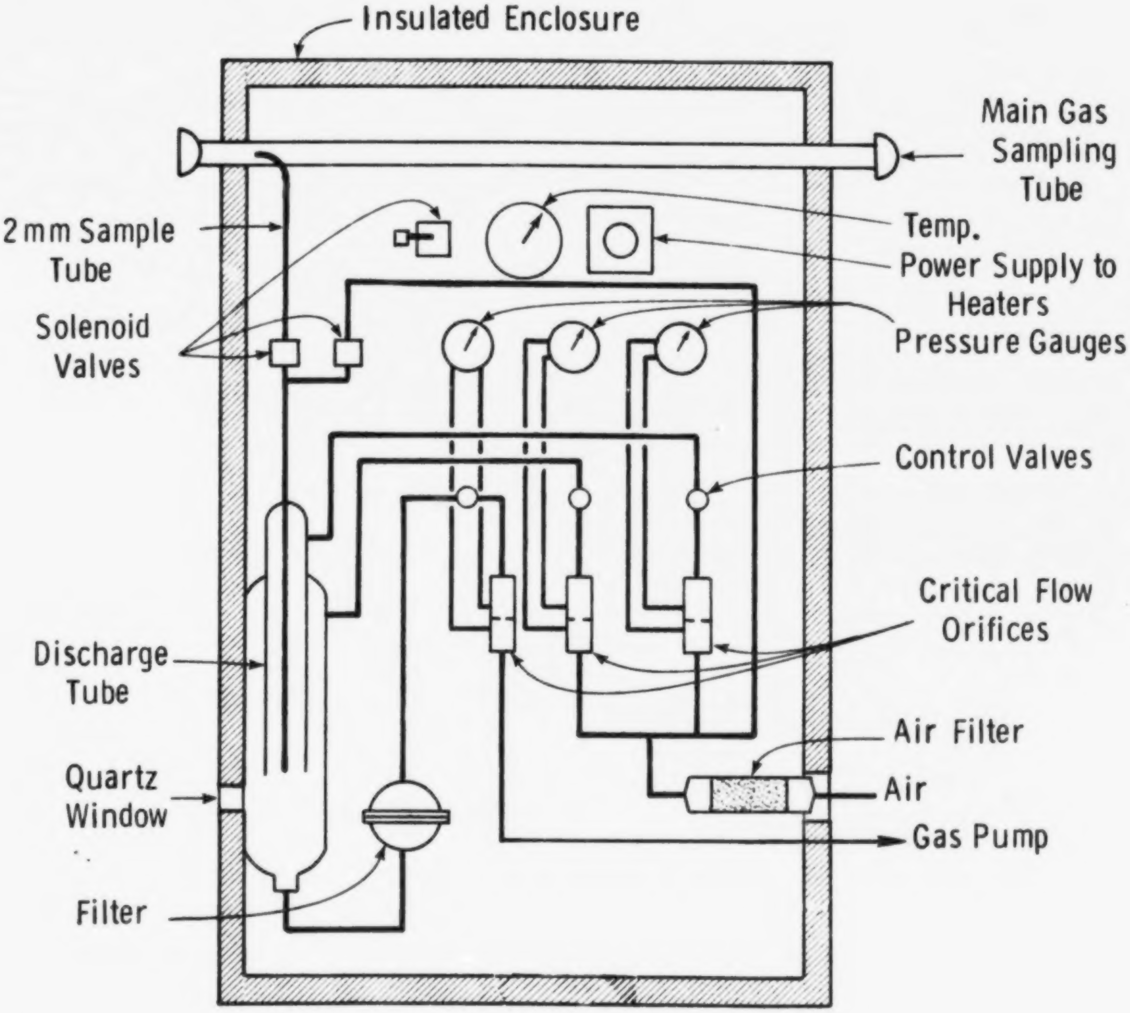
Insulated Enclosure
Main Gas Sampling Tube
2 mm Sample Tube
Temp.
Power Supply to Heaters
Solenoid Valves
Pressure Gauges
Control Valves
Critical Flow Orifices
Discharge Tube
Air Filter
Quartz Window
Air
Gas Pump
Filter

Figure 2. Be/Cd Sample Compartment.

Maspeth, New York City, New York 11378) designed and built specifically for generating RF plasmas. The unit is tunable in frequency from 15 to 50 MHz with a maximum continuous power output at the load of 2500 watts.

The temperature control system supplied with the generator was modified by adding an external heat exchanger. A circulation pump (minimum 2 gallons per hour at 30 psi with maximum 86°F water temperature), 5-gallon distilled water reservoir, and 15-gallon cooling water heat exchanger with 50 feet of one-half inch copper tubing for the distilled water were assembled. Cooling water was city tap water circulated through the 15-gallon reservoir.

Front panel terminals on the generator were provided to attach the water-cooled load coil for generating the RF plasma. The plasma was confined in a quartz tube, and a pressure cylinder, regulator, and rotameter were used to admit the plasma gas to the base of the plasma tube via a holder with tangential inlets.

The plasma shape was very important in order to get a gaseous sample into a region of excitation (ref. 11,12). A toroidal, or donut-shaped, plasma was desirable since it allowed sample to enter up the central cooler region for proper excitation. An undesirable plasma was elongated and bullet-shaped with a hot zone up the middle and cooler at the edges. With such a plasma the sample would tend to be thrown out to the cooler area along the sides of the plasma tube rather than pass through the hotter central excitation zone.

The tangential plasma gas inlet with resulting vortex flow and, in later studies, coaxial flow using concentric quartz tubes was required to form a toroidal plasma. An excitation frequency appropriate for each type of plasma gas and plasma tube diameter was also necessary.

Load coils of 3/16" and 1/4" refrigeration tubing were used. One to five turn coils were wound and used in attempts to form desirable plasmas, but three turn coils were found to be the best performers. Spacing between turns was varied from 1/16" to over 1/2" with large diameter plasma tubes. Inner diameters of the load coils were varied to match the outer diameters of the quartz tubes up to 1/2" or more clearance with the larger plasma tubes. Some miscellaneous coils shaped like cones or pancakes were also wound.

The tangentially injected plasma gas flowed through the discharge tube in a counterclockwise (CCW) direction. Coils were wound so that their ascending turns coincided with the direction of the ascending gas. In this configuration, the ground side of the load coil was nearest the plasma gas inlet. Alternatively, the turns descended CCW opposing the CCW ascending gas, such that the ground side of the load coil was in this case nearest the upper exit end of the plasma tube. No effect was observed on plasma operation. This was contrary to results of an earlier study (ref. 13).

Quartz was used for plasma tubes to resist the high temperatures of the plasma. Outside diameters were 15 mm, 20 mm, 22 mm, 25 mm, 28 mm, 32 mm, 38 mm, and 48 mm. The tubes 25 mm and smaller had 1 mm walls, while the others had 1-1/2 or 2 mm walls. All were approximately 10 to 14 inches long. All sizes except the 15 mm tube were used alone with tangential plasma gas inlet and vortex flow. The 20 mm and 28 mm tubes were used as outer tubes with a concentric inner 15 mm tube to form coaxial plasma gas flows.

The discharge tubes were mounted in two types of holders. Initial studies were performed with phenolic, aluminum, and brass holders designed for 28 mm, 38 mm, and 48 mm tubes. Later, aluminum and stainless steel holders were constructed so that sample gas could come in contact only with the stainless steel. The inner tube in the concentric assembly was 15 mm, and the outer tube was interchangeable, either 20 mm or 28 mm.

The aluminum-stainless steel holders could be used with concentric tubes or disassembled for single plasma tube studies. All holders had a provision for inserting a 6 mm diameter tube through the bottom to inject gaseous samples at high velocity into the plasma. The larger holders could be used with slightly smaller tubes wrapped with tape to provide a gas-tight fit. Concentric tube holders similar in concept have been used by several other workers (ref. 9,13), but not all have employed the great versatility of interchangeable parts used here.

5.2.1.2 Drake Radio-Transmitter Radio-Frequency Generator System

An amateur radio transmitter (Drake Model T-4XB with Drake AC-4 power supply, R. L. Drake Company, Miamisburg, Ohio 45342) with an input power of 200 watts tunable from 21 to 21.5 MHz and 28.5 to 29 MHz served as the RF source. To obtain the necessary power to sustain an RF plasma, the Drake Transmitter was used to drive a high frequency linear amplifier (Model PA70-A, Ehrhorn Technological Operations, Inc., Brooksville, Florida 33512) with a continuous power output capability of 1250 watts.

The load coil consisted of copper refrigeration tubing wound in a helical shape to conform to the outside shape of the quartz plasma type (20 mm O.D.). The quartz tube merely confines the plasma gas and substance to be excited (beryllium and cadmium in this investigation) in a defined zone. A block diagram serves to illustrate this (Figure 3).

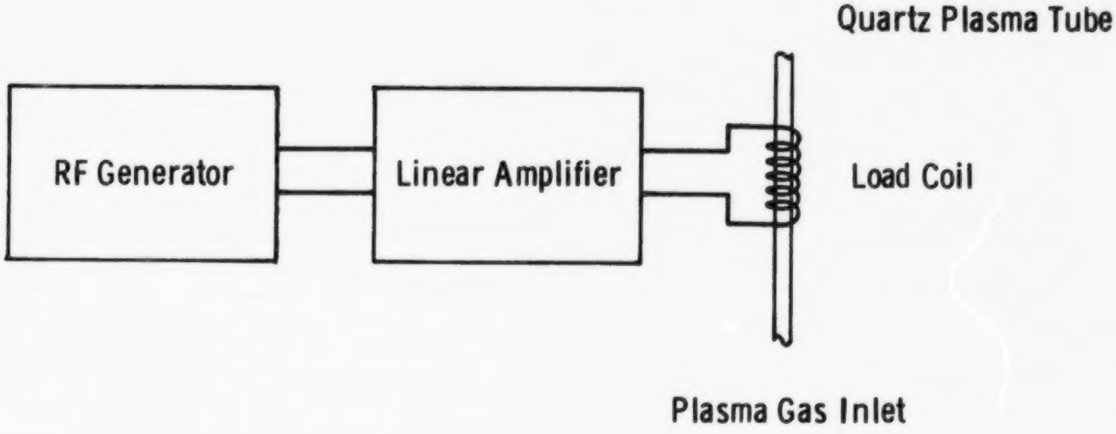
Quartz Plasma Tube
RF Generator
Linear Amplifier
Load Coil
Plasma Gas Inlet

Figure 3. Diagram of Drake Radio-Transmitter Radio-Frequency Generator System.

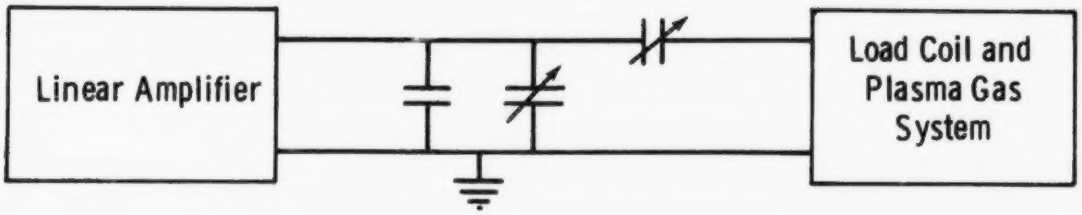
Linear Amplifier
Load Coil and Plasma Gas System

Figure 4. Diagram of Impedance Matching Network for Drake Radio-Transmitter Radio-Frequency Generator System.

To obtain efficient and maximum transfer of power from the RF generator to the load coil-plasma system, an impedance matching network is necessary. A workable network was designed and constructed as shown in Figure 4.

The output impedance of the ETO linear amplifier is approximately 50 ohms, but the input impedance of the load coil-plasma gas system is variable and depends on a number of operational parameters. Most important of these are the ease and degree of ionization of the plasma gas.

The load coil-plasma gas system can be considered to be a transformer with a multiturn primary winding (the excitation coil) and a single turn secondary (the plasma gas). Before initiating the plasma, the gas is not ionized and exhibits a high impedance which is considerably greater than 50 ohms. However, immediately after the highly ionized plasma is formed, the impedance of the load is drastically reduced to well below 50 ohms. An efficient, adjustable, matching network is required to follow the change in impedance to maintain the plasma.

To form a plasma, argon gas was passed up the 20 mm O.D. quartz tube tangentially. A tangential flow (vs. a laminar flow) pattern is advantageous because the cool, nonionized plasma gas passing rapidly near the inner tube wall prevents overheating of the quartz tube by the plasma. The formation of a toroidal-shaped plasma is also promoted with a tangential flow. Tangential flow is obtained by admitting the plasma gas through a specially machined holder at the base of the plasma tube. Argon was admitted at a flow rate of about 20 to 30 liters a minute via a pressure tank, regulator, and rotameter. The load coil (copper refrigeration tubing) was cooled by pumping distilled water continuously through an external circulation system (1/2 gal/min).

Load coils were wound using 1/8", 3/16", and 1/4" refrigeration tubing. There were about 1-1/2 turns to as many as 10 turns with the spacing between turns varied from almost touching to about 1/4". The inner diameters of the coils were 20 mm, which barely touched the quartz tube, to over 25 mm.

The plasma tube was quartz, 20 mm O.D. with a 1 mm wall thickness. Most tubes were about ten inches in length, but their length was not critical. Tube holders were made of Plexiglas and aluminum.

5.2.1.3 Monochromator and Emission Detection System

5.2.1.3.1 Jarrell-Ash 0.25-Meter Monochromator - A 0.25-meter Jarrell-Ash Model 82-410 monochromator was used as the wavelength separation device for radiation emitted from the RF or a.c. arc excited materials. It is a low cost, small size, light instrument suitable for portable or field use. The specifications are as follows:

Focal Length - 0.25 meter Ebert design

Linear Dispersion - 3.3 nm/mm with 1180 grooves/mm grating
1.65 nm/mm with 2360 grooves/mm grating

Aperture Ratio (speed) - *f*/3.5

Gratings (two supplied) - Ruled area: 64 mm x 64 mm
Replicas: 1180 grooves/mm
2360 grooves/mm

Gratings blazed at - 300 nm and 600 nm

Resolution (half-band width at 313.1 nm) - Better than 0.3 nm in First Order with 2360 grooves/mm grating with 150μ slits

Slits - Two 150 micrometer slits, fixed

Wavelength Coverage - 200 to 900 nm

5.2.1.3.2 Emission Detection System - Two RCA 1P28A photomultiplier (PM) tubes were housed in Pacific Photometrics Model 50F PM tube housings. One PM tube served as the sample tube and the other was the reference tube, as briefly described under the design concept in Section 1 of Appendix VII. A Bertran Model 602-11N power supply supplied the high voltage to the PM tube dynode chain.

An MRC designed and fabricated electrometer amplifier was used to monitor the PM tube currents. The amplifier was a differential, dual channel design arranged to accept two PM tube inputs, one due to a sample and one to a reference, and subtract the reference from the sample before display on a meter or optional strip chart recorder.

The sample channel incorporated a switch selectable range of input currents of 10^{-9} to 10^{-5} amps full scale in decade steps. Intermediate steps X1, X2, and X5 were also provided for each decade range. The reference channel was hard wired to 10^{-6} amps full scale, and a ten-turn potentiometer at its output allowed subtraction of any current from 0 to 10^{-6} amps from the sample channel. A manual zero control (10-turn potentiometer) allowed adjustment of the electrometer circuitry to zero output with no current inputs.

In addition to real time spectral measurement capabilities, the electrometer had a built-in integrator allowing accumulation of PM tube currents over a manually controlled time period.

An auto zero circuit allowed zeroing the electrometer output in the spectral mode when observing only the background of an RF plasma or a.c. arc discharge with both the sample and reference PM tubes. With no material of interest (Be or Cd) undergoing emission, both PM tube channels should be equal and the electrometer output should be zero. When operating in the integral mode, the auto zero was set first in the spectral mode. Then an "integral zero" switch position allowed manual resetting of the integrator.

The time constant of the electrometer could be chosen and an appropriate low leakage capacitor hard-wired into the final amplifier stage of the electrometer. A front-panel meter indicator served to show the electrometer output, and a back-panel recorder jack was provided to allow for permanent record keeping using a 10-mV strip chart recorder.

5.2.2 Results and Discussion

5.2.2.1 Plasma Formation With Lepel R.F. Generator System

Argon, nitrogen, air, and a gas mixture (2.7% SO_2, 15.2% CO_2, 3.1% O_2, 79% N_2) were used as coolant or plasma gas with the single or concentric tube arrangement. However, in tubes smaller than 28 mm in diameter, a plasma could be formed only with argon. The sample carrier gas was argon, nitrogen, or air. Oxygen was also used with success as a plasma gas in a single tube, and a plasma was formed using a heated injection probe and an argon-hydrogen mixture.

The plasma was easily initiated and sustained on pure argon gas, but it was impossible to initiate a plasma on any other gas or gas mixture. After a number of attempts, a 100% nitrogen, air, or artificial stack gas plasma could be sustained in a single 28 mm quart[illegible]asma tube by gradually adding these gases to the pure argon plasma and tuning the Lepel generator as the ratio of argon in the plasma decreased. Once the proper load coil, excitation frequency, and tuning procedure was familiar, it became an easy and rapid procedure to start an argon plasma and switch over to the desired plasma gas.

A well-defined toroidal plasma could be obtained with argon, but when other gases were added the plasma became elongated, smaller in diameter, and more bullet-shaped. When using air, a long tail flame extending to the open end of the plasma tube as well as a "preflame" extending to the plasma tube holder formed. A great deal of chemiluminescence was observed with the hottest area of the plasma being bluish-white and the preflame and tail flame being yellowish. With artificial stack gas, the chemiluminescence was again observed but there was more reddish color apparent in the intermediate temperature zones between the bluish and yellow zones.

The changes in plasma shape with the introduction of air, along with decreases in line-to-background ratio and line intensities, were also observed by Truitt and Robinson (ref. 14) with a radio-frequency (8 MHz) induced plasma at 4.0 kVA power. Also, NOγ-system bands appeared along with fairly strong, poorly developed O_2 bands and moderately strong, well-developed N_2 and NH bands. The emission intensity increased markedly with increasing RF power from 1.2-4.0 kVA (ref. 14).

When operating an argon plasma, the RF power level necessary to sustain the plasma was lower than with any other gas. Also, the plasma was quieter acoustically with a lower background intensity and there were less pronounced intensity fluctuations with argon.

With an air plasma, chemiluminescence was very evident. Plasma flicker was more troublesome and the radio frequency interference (RFI) and electromagnetic interference (EMI) radiated by the load coil and picked up by the electronic measuring circuitry was intolerable. Apparently the greater Lepel generator RF power levels necessary to maintain an air plasma cause excessive radiation of unwanted RF into the photomultiplier tube, electrometer, and recorder electronic systems. Figure 5 shows an emission scan of an argon-air RF plasma from 3100 Å to 3300 Å indicating the multitude of emission lines and noise in this region of the spectrum.

All grounded instrument power cords (115V, 3-wire) were isolated. The Lepel generator (requiring 230V, single phase, 3-wire power) ground was left intact (a metal shielded power cable and positive connection to utility ground) in order to comply with FCC and manufacturers specifications. The best grounding was found by connecting the cases and shields of all instruments (PMT high voltage power supply, monochromator-PMT housing, electrometer, recorder) together via separate, heavy #12 gauge copper wire and grounding them at one common point of utility ground. The Lepel utility ground was not identical to the instrument utility ground, since unsatisfactory operation resulted when the instruments were grounded to the Lepel generator case which was in turn connected separately to 230V utility ground.

The RFI and EMI radiating from the load coil (not being absorbed to operate the plasma) were eliminated with a galvanized tin U-shaped shield placed around the coil. The shield was open at the top and bottom to admit and exhaust samples and plasma gases and had a 1" diameter aperture in the side to allow passage of emission light to the monochromator and photomultiplier tube.

5.2.2.2 Plasma Formation With Drake Radio Transmitter Generator System

A good plasma was formed using the radio transmitter system and argon gas. However, careful tuning of the transmitter, amplifier, and matching network with a fixed load coil, plasma tube, and gas flow rate was absolutely necessary.

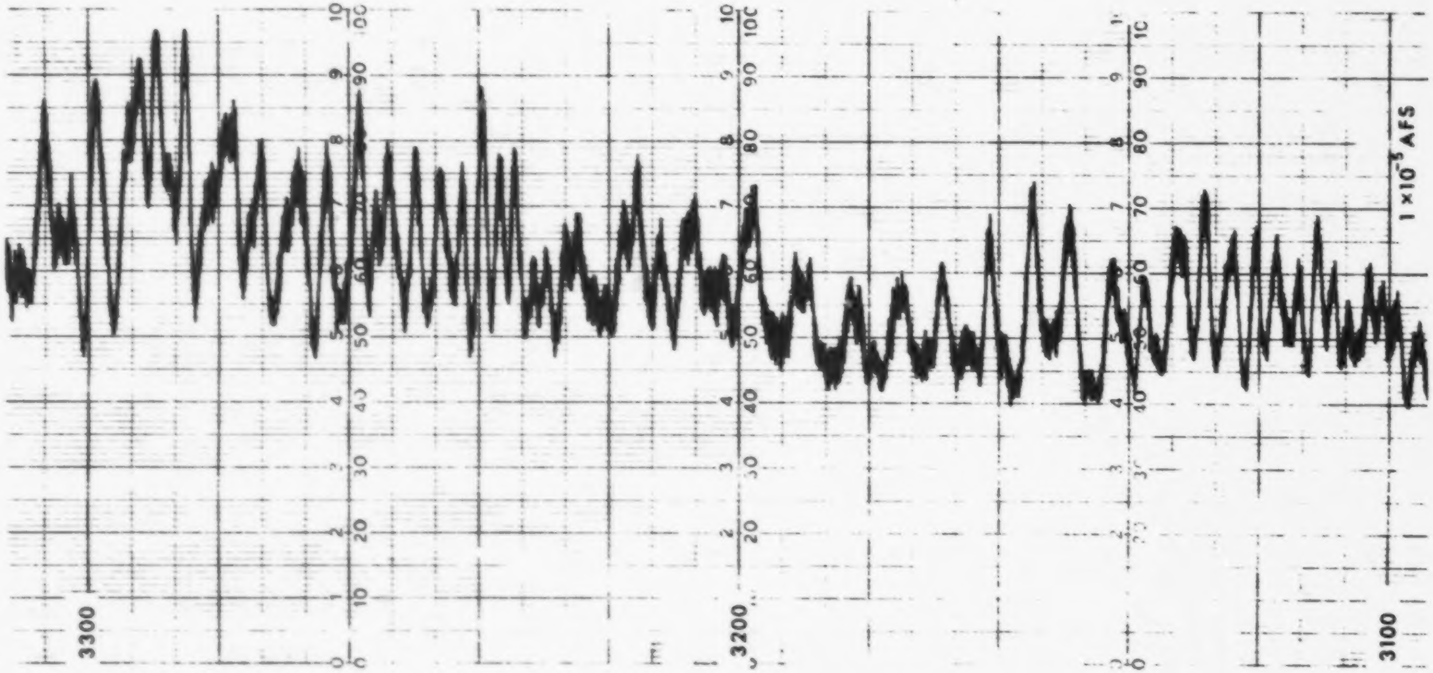

Figure 5. Scan of Emission Spectrum (3100-3300 Å) From Argon-Air RF Plasma.

Slits = 10μ
Scan Speed = 20 Å/min.
Chart Speed = 1"/min.

Argon = 26 l/min.
Air = 7.5 l/min.
1 x 10^{-5} amps full scale

Plasma operation could not be sustained in nitrogen gas. Even a small percentage of nitrogen in the argon extinguished the plasma.

The RF generator system was not powerful enough in this application to sustain anything except an argon plasma. The argon plasma was very difficult to initiate. At one point, voltages high enough to destroy a large variable air capacitor in the output tuning network of the linear amplifier were realized. The matching network was perhaps less efficient with an inductively coupled load vs. a capacitively coupled load used successfully at low power levels by other investigators (ref. 8). Since impedances changed so drastically from before to just after plasma initiation, there was simply not enough reserve power to sustain the plasma while readjusting the matching network from the high impedance, "pre-plasma" settings to the low impedance settings just after plasma formation. Many arc-like, ionization streamers appeared instead of a true, uniform plasma. Because of these operational difficulties, this approach was abandoned at an early stage.

5.2.2.3 Systems for Introducing Known Quantities of Be or Cd Into RF Plasma

Several different systems (fluidized bed, nebulizers, and vapor generators) served to introduce known concentration of cadmium, as aerosol or vapor, into the RF plasma. Each system had limitations. The major problems were related to deposition of particulate or condensed vapor on the walls and optics. The problems were greater when introducing air, than when using argon alone, because of the different plasma shape (bullet, rather than toroidal), length, temperature distribution down the pre-plasma zone, RF coupling to metal probes, and higher pressures at the base of the bullet-shaped plasma. The most efficient method of delivering the calibration specimen was by vaporizing cadmium metal from a copper tipped probe which was maintained at 210-220°C and which provided close delivery at a high injection velocity. Delivery of sample to the air or air-argon plasma from other systems resulted in little penetration at the base of the plasma and in a sample flow pattern around the periphery of the plasma at the tube walls where the pressure was less and where, unfortunately, the temperature was also lower.

Typical problems and some solutions, are described in the following sub-sections. Cadmium was chosen for the preliminary laboratory studies because it is less toxic than beryllium.

5.2.2.3.1 Pneumatic Aerosol Generator - A pneumatic aerosol nebulizer (Bennett #2814 Twin Nebulizer, Bennett Respiration Products, Inc., 1639 Eleventh Street, Santa Monica, California)driven by argon gas was used with cadmium solutions to produce a spray of known cadmium concentration. Difficulties in steady plasma operation were experienced when the aerosol entered the plasma. The water droplets absorbed great amounts of RF energy on vaporizing and disassociating in the plasma and the greater pressures developed on heating the liquid (small volume) droplets to disassociated atoms (large volume) caused intolerable plasma flicker and unsteady plasma operation.

5.2.2.3.2 Desolvating Apparatus - A desolvating apparatus similar to that used earlier by Veillon (ref. 15) was used; however, the larger droplets produced by the pneumatic nebulizer (vs. the ultrasonic nebulizer used by Veillon) were not as effectively desolvated. A Beckman Type 2010 total consumption type atomizer burner served as an aerosol generator, but produced droplets larger than those of the Bennett nebulizer. A large proportion of the solid aerosol produced by desolvating the liquid droplets crystallized on the apparatus walls.

5.2.2.3.3 Motor Driven Syringe - A motor driven syringe (Model 335, Sage Instruments, Inc., White Plains, New York) was used to inject known volumes and concentrations of cadmium in aqueous solutions. Difficulties were encountered when attempts were made to get sufficiently close to the plasma to inject the aqueous sample. The solution vaporized unevenly resulting in intermittent injection rates and ultimately the stainless steel syringe needle fused from the heat of the plasma.

5.2.2.3.4 Cadmium Metal Vaporizers - Since the volatility of cadmium metal (and a number of cadmium and beryllium salts) is rather high (cadmium b.p. 767°C and a vapor pressure of approximately 2×10^{-4} mm @ 183°C), the possibility of forming a metal vapor by passing a carrier gas (argon @ 1 l/min.) over a heated cadmium metal was explored. Several configurations were tried, but the most efficient system was a stainless steel delivery tube (1.5 mm I.D.) jacketed with concentric tubes of copper to permit handling of a heat exchanging fluid. With this probe system, the injector tip could be placed directly into the base of the plasma, which enveloped the injector tip. A diagram of the probe is shown in Figure 6.

The innermost tube which carries the sample gas is made of 3-mm stainless steel with a 1.5-mm I.D. central channel. The two other concentric tubes are 4.5 mm and 6 mm O.D. copper. All tubes were silver soldered into an upper copper tip and a copper block at the bottom for rigidity and getting coolant in and out. A container made of black iron pipe and fittings wrapped with a Variac controlled heating tape and insulation was used to generate cadmium metal vapor to inject into the plasma via the injection probe. Reagent grade cadmium metal filings served as a source of cadmium vapor.

By using glycerol (b.p. 290°C) as the heat exchanger fluid, the probe could be maintained at 210-240°C by circulating glycerol from an external constant temperature bath. With pot temperatures

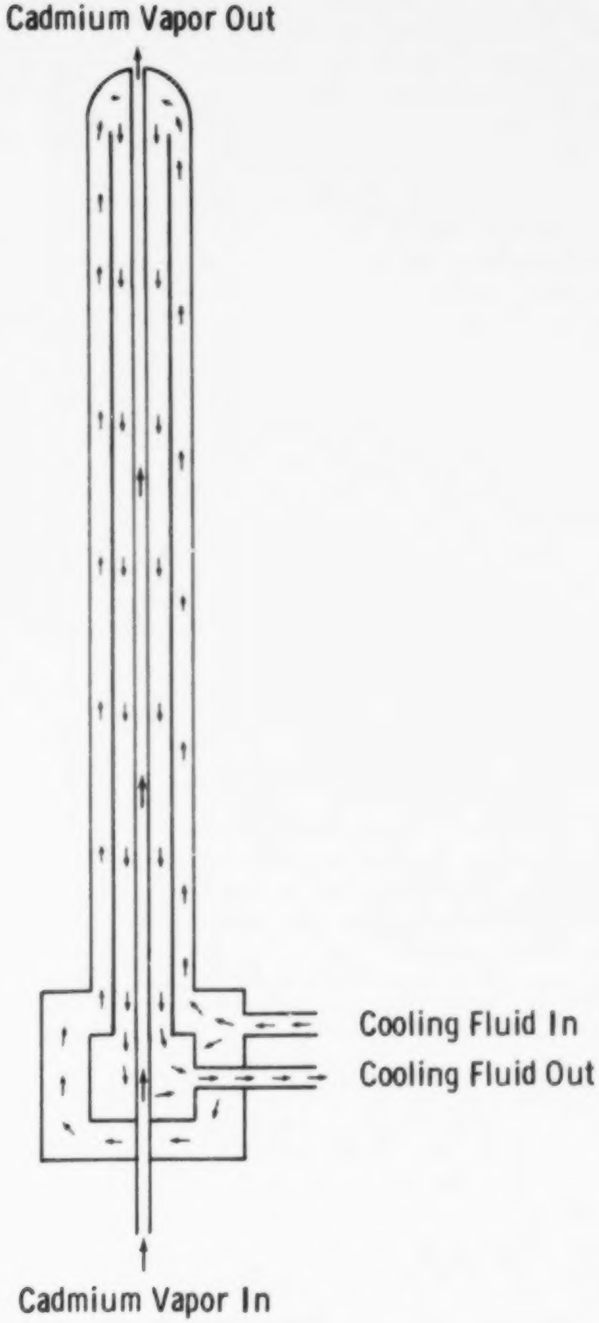
Cadmium Vapor Out
Cooling Fluid In
Cooling Fluid Out
Cadmium Vapor In

Figure 6. Diagram of Cadmium Metal Vaporizer Probe for Injecting Cadmium Metal Vapor Into RF Plasma.

of 180-200°C, sufficient cadmium vapor can be obtained with no deposition on the injector probe.

A minor disadvantage with using glycerol was the difficult start-up with room temperature, viscous glycerol. The probe passages were restricted to such an extent that viscous fluids would pass only with difficulty, but once operating temperature and initial circulation were achieved, the low viscosity of hot glycerol presented no problems.

The metal vapor injecting probe was used only with cadmium metal; however, volatile beryllium or cadmium salts could just as easily have been used. By using controlled temperatures, carefully regulated carrier gas flow rates, and careful choice of volatile salts, beryllium or cadmium or both simultaneously could be injected into the plasma in known amounts to calibrate the instrument.

Calibration of the quantity of cadmium delivered by the probe was accomplished by atomic absorption spectrophotometric analyses of cadmium collected in impingers over time periods extending up to 16 hours. At the flow rates of the plasma gases, the cadmium generated in this system would produce concentrations in the plasma at the 10 µg Cd/m^3 level.

For long term operation, the trace quantities of oxygen in the argon carrier gas should be removed to prevent oxidation of the cadmium metal in the reservoir. This is readily accomplished by passing the carrier gas through freshly reduced copper turnings maintained at 500°C.

5.2.2.4 Detection of Cadmium With Radio-Frequency Plasma Emission Spectroscopy

Laboratory experiments using the cadmium vaporizer system and the Lepel RF generator were conducted to determine the feasibility of employing an RF induced plasma and emission spectroscopy for monitoring cadmium continuously in a flowing stream of air. Initially, experiments were conducted with argon and, finally, with argon-air mixtures. Two types of plasmas were evaluated: (I) induction coupled RF plasma formed with a mixture of sample and sheath gases, and (II) induction coupled RF plasma jet formed with sample gas alone. The former is produced at much higher RF power and flow rates than the latter, but the latter is quieter and yields lower detection limits.

All the major cadmium emission lines were observed including 2288 Å, 2980 Å, 3261 Å, 3404 Å, 3466 Å, and 3610 Å, and the 2288 Å and 3261 Å emission lines were found to be most sensitive and approximately equal in intensity.

5.2.2.4.1 Cadmium Detection With Type I RF Plasma - In an induction coupled RF plasma (Type I) with pure argon (24 l/min), cadmium emission (3261 Å) was detected photoelectronically by measuring the emission signal directly. Without signal integration, the photoelectric system produced a detection limit better than 10 μg Cd/m^3 of argon. The 10 μg Cd/m^3 value was established by collecting the Cd for approximately 16 hours in impingers containing 10% hydrochloric acid and by performing analyses of the collected specimens with atomic absorption spectrophotometry.

The intensity of cadmium emission at this wavelength with a nitrogen plasma was reduced by a factor of 5 when compared to the emission intensity in the argon plasma. Approximately the same reduction in emission was observed when an oxygen plasma was used.

After introducing a small quantity of air (<0.5 l/min.) into the plasma gas (total flow rate of 20 l/min.), no emission spectrum for cadmium, introduced either using the water solution nebulizer (set to deliver up to 0.01 g Cd/m^3 of air) or as cadmium metal vapor (up to 0.6 g Cd/m^3 of air) generated by heating cadmium metal to its melting point (321°C), was detected photoelectronically at 3261 Å or during a scan from 2000 Å to 4000 Å. The effect was also observed visually by dramatic changes in color of the plasma from a definite blue color with a pure argon matrix to a complete loss of the blue color with the addition of approximately 2% air.

Finally, several grams of cadmium oxide powder were placed in the bottom of the plasma tube holder and blown up into the plasma. With an argon plasma, an intense blue color was seen visually, but when air was added, the blue color disappeared immediately and almost completely. Only a very slight hint of blue color was evident by visual examination. A similar experiment was performed with cobalt oxide and iron oxide powders and the same result was observed visually.

With the air addition, (a) the plasma becomes elongated, (b) flame flutter occurs, (c) optical noise increases, (d) turbulence is greater, (e) toroidal shape is lost, (f) background emission is enhanced, and (g) no cadmium emission lines are observed. In addition, a wavelength scan of the elongated plasma at various positions in the preflame, central flame, and tail-flame sections of the plasma yielded neither cadmium emission lines, nor distinct line or band spectra correlatable with CdO molecular spectral emission.

Movement of the sample injection tube to various positions in the plasma, i.e., from plasma base center to a position nearer the cooler wall, but still at plasma base, or from the plasma base and preflame zone to the tail-flame, did not help.

5.2.2.4.2 Cadmium Detection With Type II RF Plasma - A small plasma jet flame (Type II RF Plasma) can be produced at the tip of the sample injection probe, when the probe is positioned in the induction coil zone and the only source of argon is the small argon-sample flow (2 l/min.) through the injection probe. The induction coil, quartz tube, and sample injection have the same configuration as during normal plasma operation, but the matrix gas (argon @ 20 l/min.) is not present.

This phenomenon has not been reported with an inductively coupled plasma, but it is similar to that reported earlier (ref. 8) using capacitively coupled plasma probes. The jet was about 2 or 3 mm in diameter, which was approximately the size of the internal diameter of the central stainless steel injection probe tube, and about 20-25 mm tall. It appeared to be the same color as a typical argon plasma.

The plasma jet is produced with pure argon or with up to 10% hydrogen in argon. However, it was not generated with nitrogen or air mixed with argon. Very little RF power was necessary to maintain the plasma jet. It operates silently and does not flicker, but RF interference and electromagnetic interference are proportionally greater in the electronic measurement system considering the very low power input to maintain the jet.

The best limit of detection of cadmium (0.4 μg/m^3) (without signal integration) in an RF plasma was obtained by using a pure argon plasma jet and by measuring the intensity of the cadmium emission line at 3261 Å.

5.2.3 Conclusions - Radio-Frequency Excited Optical Emission Spectroscopy

This study showed that although radio-frequency induced plasma temperatures as high as 20,000°K can be attained at atmospheric pressure, the detection of the emission spectra of trace metals is extremely difficult when using air or air-enriched argon as the matrix gas. The plasma temperatures are sufficiently high to vaporize most refractory compounds and the excitation energies (up to 25 electron volts) provide the necessary electronic excitation to produce excellent emission spectra with argon as the matrix. But with air in the plasma matrix, the plasma shape becomes distorted, increased background emission spectra are obtained, and the line intensities of the element being determined are diminished. As a result, direct analytical determinations of cadmium in air matrices were not possible even at levels in excess of 1000 μg/m^3.

Although several possible solutions to the air effect problem with RF induced plasma can be suggested, considerable development work would be required to establish feasibility. Also, the cost and time factors, and the dilution effects for the actual monitoring measurements may become excessive. Possible approaches include removal of oxygen or reaction of oxygen to form relatively stable oxide (CO, CO_2, H_2O, or metal oxide) and incorporation of additives to inhibit nitrogen-oxygen free radical reactions and metal-oxygen compound formation, or to change the ionization potential in selected plasma zones.

The most promising additive approach would be to incorporate a free radical scavenger to inhibit the nitrogen-oxygen reactions which produce the background spectral emission due to chemiluminescence. However, so little work has been done to date, that the potential degree of success cannot be estimated. Also, although the chemiluminescence may be eliminated, the other air effects may prevent attainment of sufficient line to background signal ratios. Complete removal of oxygen is the only assured successful solution to the problem of the air effects but also is the most impractical considering the large volumes (2-40 l/min) of sample gas that must be handled.

After reviewing the results obtained with the radio-frequency induced plasma and after discussion with Drs. V. A. Fassel (Iowa State University), T. B. Reed (MIT), and R. Mavrodineanu (NBS), we have concluded that a radio-frequency induced total air plasma or an argon plasma with moderate percentage of air which will provide for detecting trace quantities of cadmium in air may be attainable eventually, but not at the present state-of-the-art. By using auxiliary magnetic fields to restrict the plasma size and to control its shape a more concentrated source of optical emission spectra may be obtained; unwanted background emission spectra may be controlled by employing selected additives. In addition, use of metal oxide molecular spectra or spectral lines characteristic of more energetic transitions, which would be affected to a lesser degree by background interferences, may be developed. The discrimination of band and line spectra from the background may be further enhanced by modulating the analytical signal and using a synchronous detector, or lock-in amplifier, to extract the weak analytical signals from intense spectral background interference or from optical or electronic noise.

Modulation can be accomplished by several techniques, including modulation of: (a) sample introduction, (b) wavelength, and (c) two excitation sources, with and without analyte.

Signal modulation of sample introduction is potentially useful but less practical than other techniques. By rapidly admitting sample, then completely shutting it off (or by rapidly alternating between sample and blank), one can synchronously detect the difference between the emission due to the sample and that when no sample is present. The major problem is to design a system with valves and other hardware to alternately, rapidly start and stop sample introduction to the analytical excitation device.

Sample background corrections made by wavelength modulation techniques are most useful when the analytical line is buried in a large amount of background or when the analytical line falls on the shoulder of a large peak of another species present. A rotated or wobbled quartz plate placed just in front of the exit slit of the monochromator refracts the light falling on the exit slit. The result is a rapid back and forth scan over a narrow band of the spectrum centered on the wavelength of the line of interest. Rains (ref. 17) has shown this gives the first derivative of the normal output of wavelength vs. time of a scanning spectrometer.

A mechanical mirror-chopper could be used to direct the emission from two identical excitation sources, which excite emission from stack gas and particulate and from stack gas alone. A filter system would have to be used to remove particulate from the reference stream, and obviously, the system would only be used in cases where the analyte is nonvolatile or can be chemically or physically removed. A lock-in amplifier would be used to demodulate the resultant signal.

The choice of modulating technique would depend on the nature of the interference. Wavelength modulation would be the most useful for minimizing spectral background interferences.

5.3 Arc Excited Optical Emission Spectroscopy

The most successful means of determining beryllium continuously in a flowing stream of air (40 l/min.) from a beryllia manufacturing facility was accomplished by Webb, et al. (Appendix II, Section 4.1.1). By using an intermittent DC arc, 1 μg Be/m^3 was detected with sampling and analysis times of 20-60 seconds. No significant particle size effects were observed for particles of up to 20 microns for beryllia and up to 85 microns for the metal. The particulate was primarily beryllium containing material and thus the total particulate loading in the sample stream was low. The common elements normally found in atmospheric dust, namely calcium, aluminum, silicon, iron and sodium do not affect the reading of the monitor even when they are present as a visible cloud.

Because of the failure to detect cadmium with radiofrequency excited optical emission spectroscopy, a small program was devoted to determine the feasibility of using a Webb-type system for detecting beryllium in power plant emissions.

5.3.1 Instrumentation

Except for the arc discharge cell and the arc power supply, the equipment was the same as that used with the RF excited optical emission equipment. However, in some tests, a second separate monochromator was used in the reference system to aid in identifying the background emission problems.

5.3.1.1 Arc Discharge Cell

The discharge cell employed in the Webb-Harwell monitor (Appendix II, Section 4.1.1) was obtained on loan and a duplicate was fabricated by Monsanto Research Corporation. The original Webb cell was machined from Sindanyo, a high density asbestos material, and the MRC cell was fabricated from Electrobestos, an asbestos material used in high voltage applications. A diagram of the discharge cell is shown in Figure 7. The critical feature of the cell design is the flow pattern to the arc discharge zone.

Several types of electrodes were tested. Copper wire (14B&S gauge) conducted the most current without heating, but the wear rate was excessive. Platinum electrodes could not carry as much current before heating, and erosion was fairly rapid, requiring one or more adjustments per day. Platinum-iridium electrodes were better since they could be used as much as eight hours at low power levels before requiring adjustment.

5.3.1.2 Arc Discharge Power Supply

Because of time limitations, the fabrication of an intermittent DC arc power supply described by Webb could not be completed. Tests were performed with an AC arc system based on a luminous transformer (neon sign power supply) modified with a 0.01 microfarad (50 KV) capacitor across the transformer secondary to transfer maximum energy to the arc. With 115 VAC supplied to the transformer primary, the secondary supplies alternating current (AC) at 15,000 volts and 60 milliamperes (MA), or 900 VA. This system differs from that proposed by Webb in that it is high voltage, low current AC arc rather than low voltage, high current triggered direct current (DC) arc.

5.3.1.3 Calibration Systems

To generate a beryllium or cadmium aerosol, electrodes incorporating these metals were operated in the Webb cell. With the Webb cell placed before and in series with the MRC cell, air drawn through both cells carried metal aerosol into the MRC cell for excitation. A diagram of the system is shown in Appendix VII, Section 2.6.2. Cadmium aerosol was generated by reagent cadmium metal formed into a suitable electrode or by a 14-gauge silver soldering alloy rod containing 18% cadmium, 26% copper, 35% silver, and 21% zinc, and beryllium aerosol was generated by a 3% beryllium-97% copper alloy in 3/32" diameter or 3/16" diameter rod form.

In addition, the Bennett nebulizer discussed with the RF plasma studies was used to form beryllium and cadmium aerosols from aqueous solutions. The heated injector probe from the RF plasma work was found to inject insufficient cadmium into the arc to permit detection.

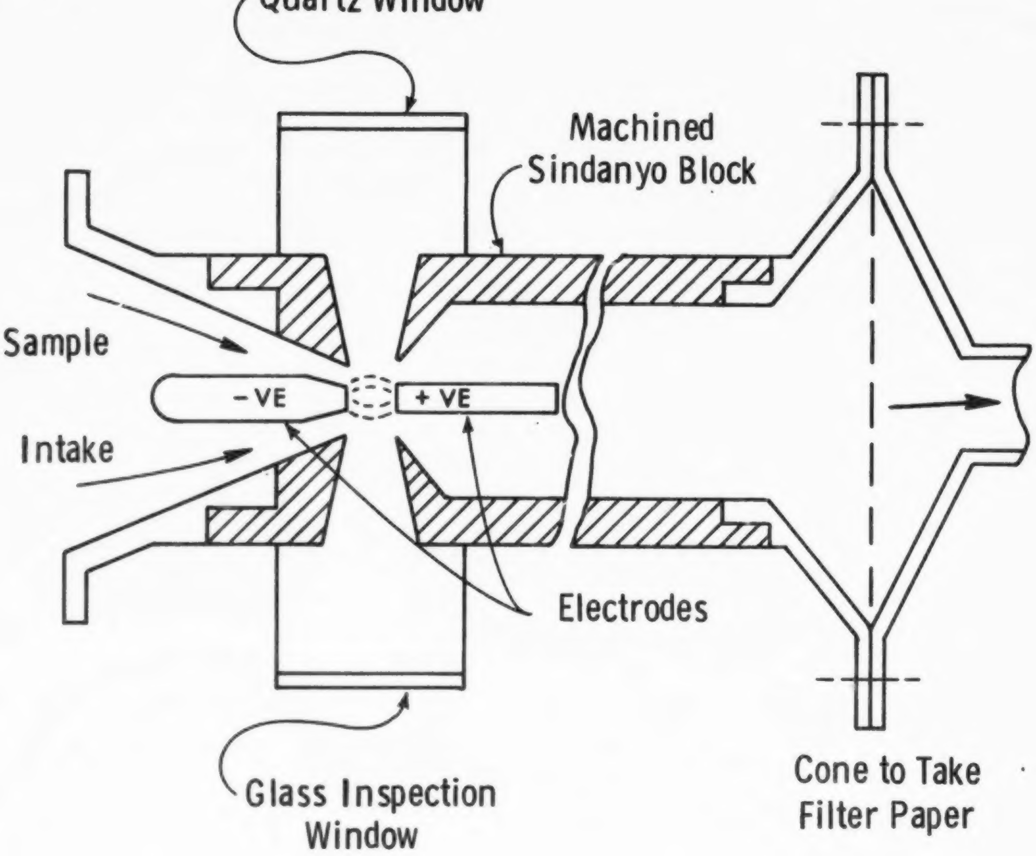
Quartz Window
Machined Sindanyo Block
Sample
Intake
−VE
+VE
Electrodes
Glass Inspection Window
Cone to Take Filter Paper

Figure 7. Diagram of Webb-Type Arc Discharge Chamber.

5.3.2 Laboratory Studies

Limitations of time precluded an in-depth evaluation of the Webb type approach. A laboratory feasibility study was conducted to establish whether the modified Webb system could be used for field applications, e.g., analyses of power plant emissions.

Contrary to results with the RF plasma, water injected into the arc did not interfere with its operation, and the resulting spectrum had a low background with no major interferences. In the high voltage, low current, alternating current arc, beryllium was more sensitive to analysis by emission than was cadmium. The limit of detection for beryllium by direct spectral intensity measurement(no integration) was the same as Webb had measured, 1 μg/m³, but that for cadmium was several times higher, >80 μg/m³.

Figure 8 shows calibration of the Webb-type arc cell with nebulized 1000 ppm aqueous solution of Be, as $Be(NO_3)_2$. Figure 9 is a calibration curve for the data derived from Figure 8. The response is neither a linear, nor a logarithmic function of concentration. These deviations indicate the possibility of quenching or poor excitation effects and suggest the need for additional power or an auxiliary heating arc system. Better improvement may be evident with the Webb intermittent DC arc, rather than the AC arc as used in this study.

Spectral scans of about 10 Å to 20 Å including all the major beryllium and cadmium emission lines (M.I.T. Tables) were made to determine the optimum emission wavelength. The wavelength positions of these have been confirmed with similar scans using a Be or a Cd hollow cathode lamp source. The best beryllium emission line is the 3130-3131 Å doublet. The optimum cadmium emission line is probably 2288 or 3261 Å; however, low sensitivities observed at all cadmium wavelengths prompted devoting full efforts to the beryllium analysis.

Figures 10, 11 and 12 show scans of the emission spectra obtained with the Webb-type cell (2000 Å to 4000 Å) for lab air, lab air plus 10,000 ppm Cd solution (nebulized into the air) and lab air plus Be emitted from a second cell containing two 3% Be-97% Cu electrodes. Figures 9 and 10 are essentially the same, indicating that no Cd emission is being detected at this concentration (>80 μg/m³) with conditions optimized for beryllium. Unfortunately, method development time was not available to optimize the instrument conditions for cadmium.

On Figure 12, the unresolved 3130-3131 Å Be doublet appearing as a single line is marked along with a pair of Cu lines. Be concentration is ∿30 μg/m³. A comparison of spectra of aqueous solutions to spectra of laboratory air show no water interferences.

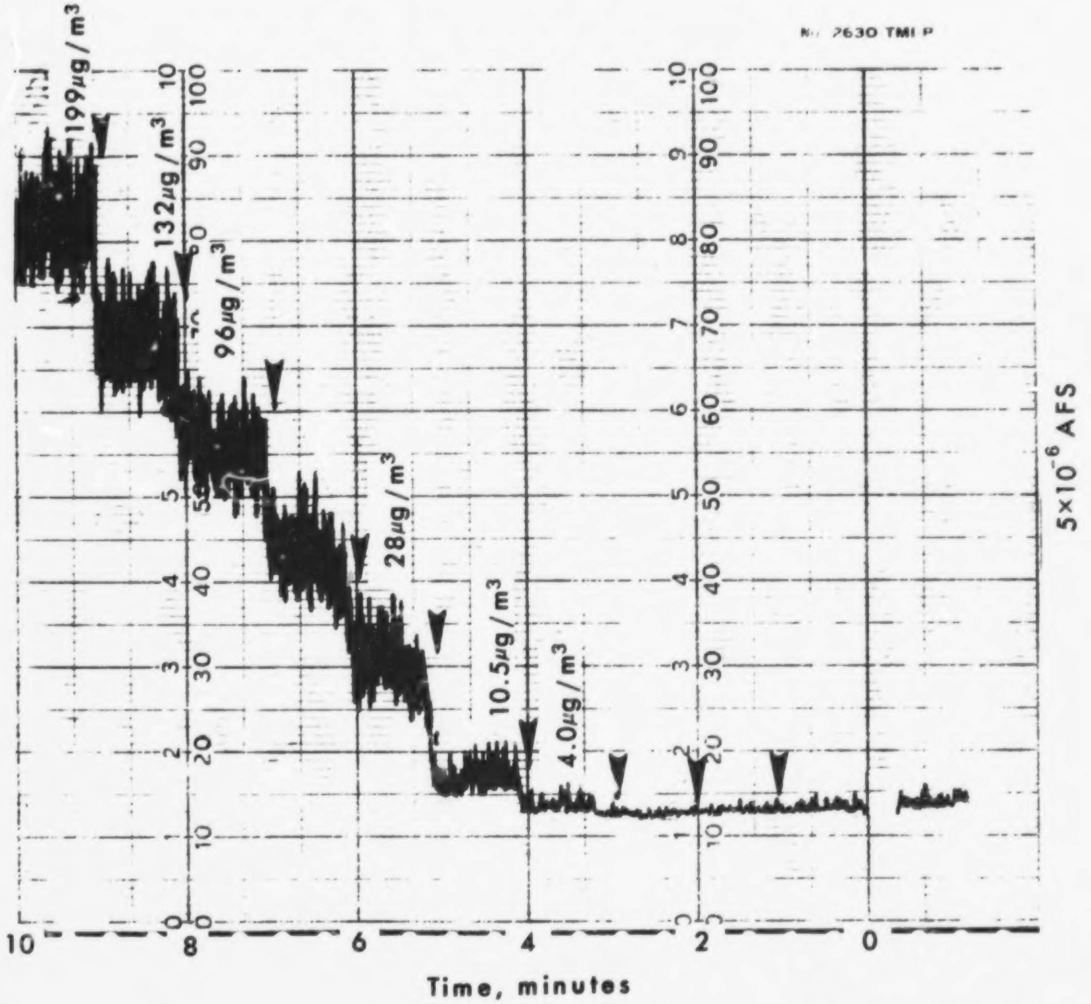

Figure 8. Emission Intensity at 3131 Å for Webb-Type Arc Cell.

Excitation of various concentrations of Be containing aerosol in argon. Arrows indicate flow rate changes. [Aerosol produced by nebulizing aqueous $Be(NO_3)_2$ solution.]

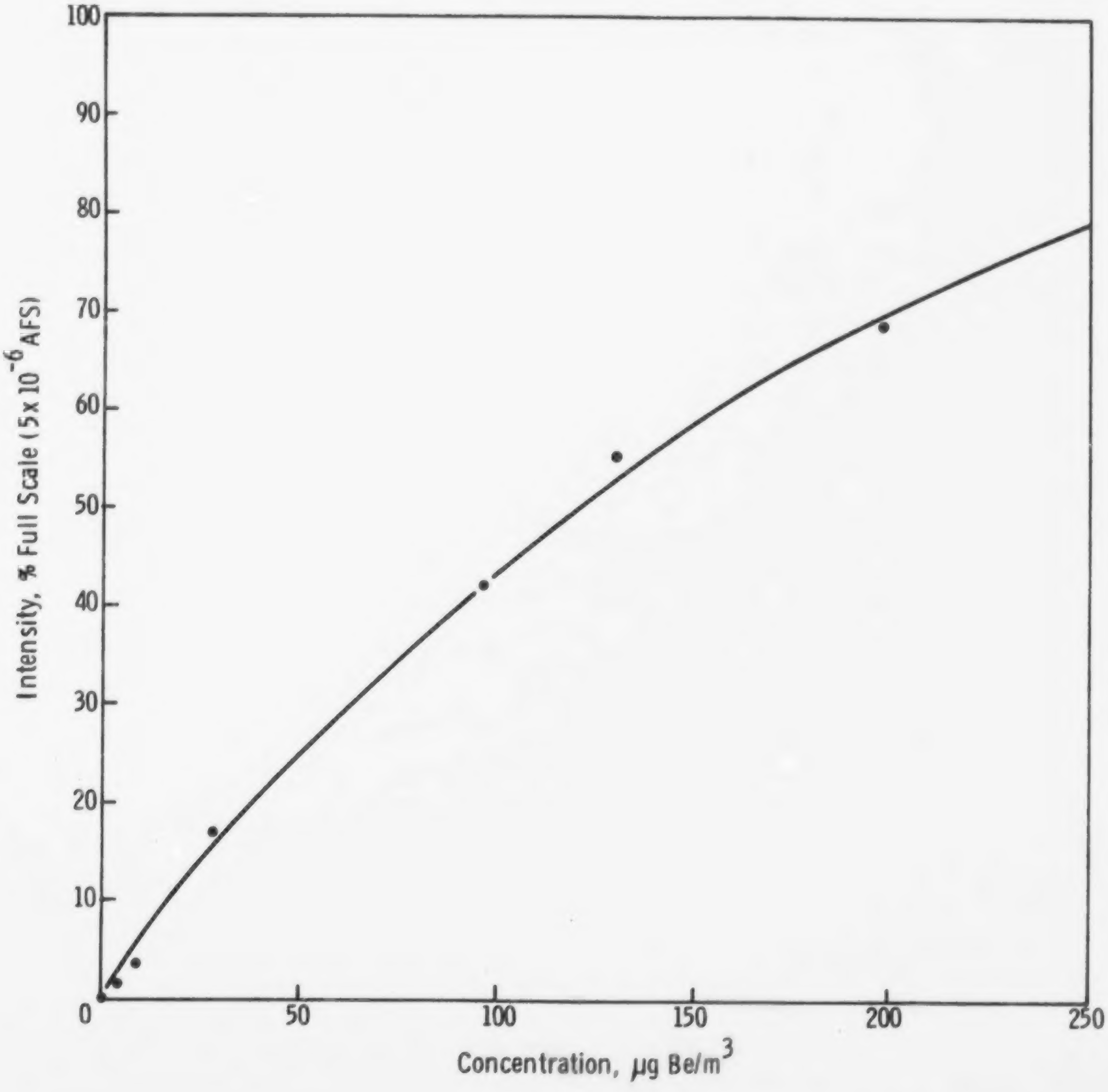

Figure 9. Calibration Curve - Be (3131 Å) Emission From Webb Arc Cell Using Nebulized 1000 ppm Aqueous $Be(NO_3)_2$ Solution and Variable Carrier Gas Flow Rates.

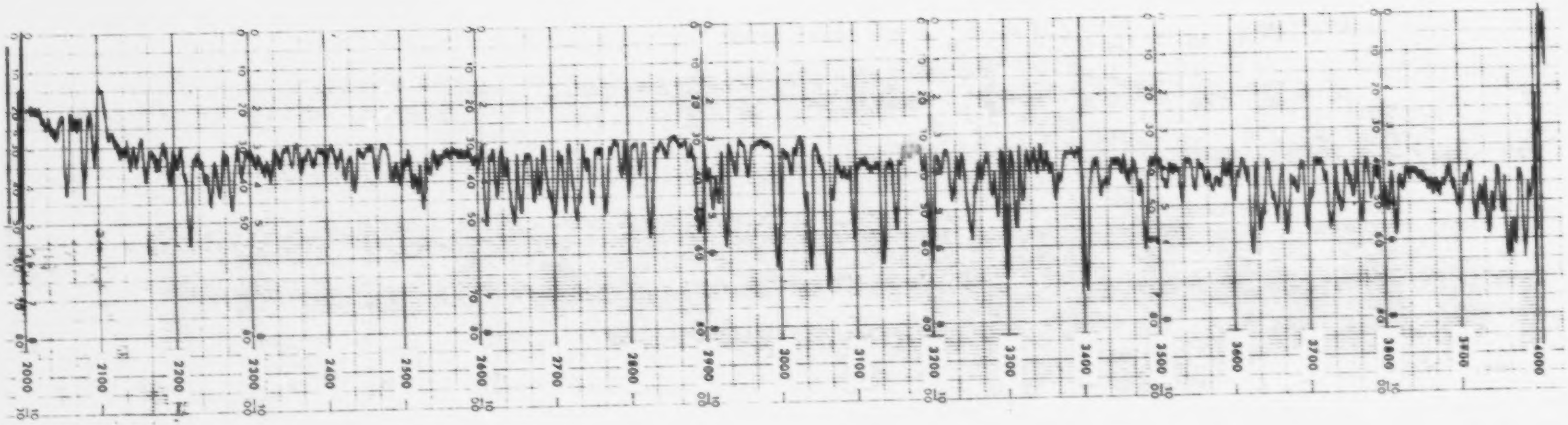

Figure 10. Scan of Emission Spectrum (2000-4000 Å) of Laboratory Air Using Webb-Type Arc Cell.

25μ Slits
50 Å/Min. Scan Speed
5 x 10^{-6} Amps Full Scale

Pt Electrodes
Variac - 75 Volts
Electrode Spacing - 2 mm

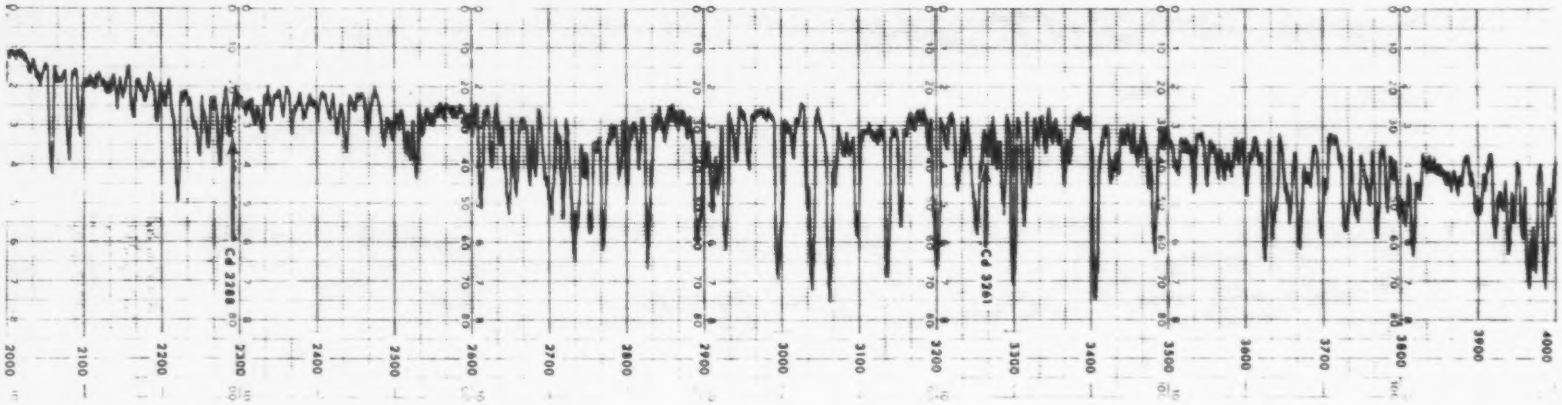

Figure 11. Scan of Emission Spectrum (2000-4000 Å) From Webb-Type Arc Cell.

[Sample is lab air plus Cd from a 10,000 ppm solution nebulized into the arc (>80 μg/m³).]

25μ Slits	Pt Electrodes
50 Å/Min. Scan Speed	Varian - 75 Volts
5 x 10^{-6} Amps Full Scale	Electrode Spacing - 2 mm

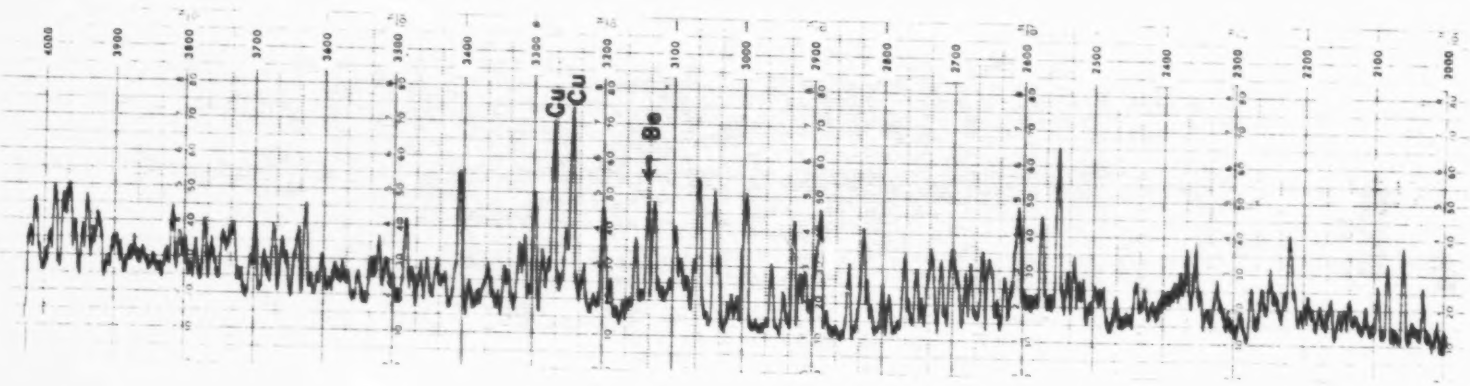

Figure 12. Scan of Emissi᠁n Spectrum (2000-4000 Å) From Webb-Type Arc Cell.
[Sample is lab air plus Be from a set of 3% Be-97% Cu electrodes.]

25μ Slits	Pt Electrodes
50 Å/Min. Scan Speed	Variac - 75 Volts
5 x 10^{-6} Amps Full Scale	Electrode Spacing - 2 mm

For preliminary laboratory studies, a second monochromator and phototube system was used in conjunction with the dual channel electrometer so that a background correction can be obtained for fluctuations in the arc emission. This presently works best with the reference monochromator set on the background emission near the 3130-3131 Å Be lines.

Slit widths have been varied to determine the optimum instrument response and this is about 5 micrometers with the intense background observed. With slits of 5 μm, 7.5 μm, and 10 μm, the signal to noise ratio around the 3130-3131 Å Be line degrades from about 10 to 6 to 2.5, respectively, with Be concentrations of 9 μg/m^3.

Maximum wear occurs with large electrode gaps and/or high input voltages from the Variac-controlled neon tube transformer. Most experimentation has been with the electrode gap at about 3 to 6 mm and the Variac input voltage about 60 volts.

An artificial stack gas containing carbon dioxide and sulfur dioxide does not interfere with Be emission. Water vapor from droplets generated in a pneumatic nebulizer does not interfere, and little or no OH emission occurs in the 3100 Å to 3200 Å region of the spectrum with air, stack gas, or the nebulized droplets.

Fly ash was introduced with few adverse effects except that in excessive amounts the electrodes seem to coat up and become unsteady. It was difficult to add the fly ash in an even, steady flow. No interferences were noted and only a small memory effect is observed when viewing the Be 3130-3131 Å line.

A filter was employed immediately downstream from the analytical electrodes in the MRC cell, and samples collected and analyzed by atomic absorption spectrophotometry were used to confirm the aerosol concentrations.

Since the sensitivity to beryllium was several times that of cadmium and since Webb had analyzed beryllium with a similar system, the decision was made to concentrate on the analysis of beryllium alone. The 3130.42-3131.07 Å doublet beryllium emission line was used for the analytical measurements. An alternate analytical Be emission line is 2348.61 Å. Although Webb et al, (ref. 1,2) reported a positive magnesium interference at 3130 Å, in which 1 mg Mg/m^3 gives a reading approximately equivalent to 1 μg Be/m^3, this interference was not observed with the fly ash matrix in this study. It is notable that the nearest spectral lines for Mg are 3104 Å and 3229 Å, which are well resolved from the 3130 Å Be lines with the present optical system. The interference, if it exists, is not a direct spectral interference and must arise from another mechanism.

Laboratory feasibility studies showed no air or water spectral interferences as had been experienced with plasma operation, but after continuous operation with aqueous aerosols, absorbed water increased the conductivity of the asbestos and it became more difficult to maintain a high power arc. Electrode wear was a problem, but this was partially solved by the use of more durable platinum-iridium alloy, and there was no spectral interference with the beryllium and cadmium. Resistance heating of the electrodes caused a diminished arc, but this could be remedied by better arc design or by using larger diameter electrodes.

6. FIELD TEST OF PROTOTYPE

Field studies with the arc-discharge emission spectroscopy system were conducted in a semi-permanent, air-conditioned shed with adequate power and stack sampling facilities on the roof of a power station. Effluent gases from the newest and most modern boiler at the site were sampled. Stack gas is delivered to the laboratory with a five-horsepower blower through a series of heated, insulated two-inch pipes. The sample is drawn from a duct, which is located after the mechanical and electrical precipitators and before the I.D. fan. The boiler tested supplies steam to a 140 megawatt generator.

Figure 13 presents a schematic layout of the field test facility located on the roof of the power plant. Figure 14 shows the top front and side views of the delivery line and blower installation used to draw samples from ducting before the I.D. fans from either of two boilers. The two sample lines joined before entering the high pressure blower, located atop the elevator shaft. The blower was capable of delivering 100 cfm of 300°F gas at an increase of 22-inches W.G. Since the sample points were at a negative 15-inch W.G., the effective pressure of the gas downstream of the blower was 7-inches W.G. The 2-inch diameter Schedule 40 carbon steel delivery line carried the sample from the blower down to the power plant roof, about 32 feet below. All sections of the delivery line and blower were heated and insulated. The entire system was weatherproofed.

A 10-ft x 14-ft prefabricated steel shed is installed on the roof. Figure 15 is a picture of the power plant test facility showing the blower, delivery line and the exterior of the shed with a 23,000 Btu air conditioner installed in one of the doors.

Numerous difficulties were encountered immediately after adding stack gas containing particulate to the cell. The emission intensity from the arc decreased and the arc glow was observed to change from brilliant white light to a duller red glow. The red glow was not observed in the laboratory studies with artificial stack gas or with fly ash when tested separately. It may occur only with both present. A scan of the emission spectrum of the stack gas showed some emission bands not observed in the laboratory studies, but no identifications were made.

Particulate matter in the stack gas built up rapidly on inner walls of the cell and the electrode holder assemblies. Examination of the cooled electrodes showed the formation of five to ten small glasslike fused beads on both electrodes within a few minutes of sampling. The AC arc does not provide sufficient energy to vaporize the fly ash.

The emission spectrum obtained for the beryllium aerosol generated with the Be-Cu electrodes showed an unresolved doublet

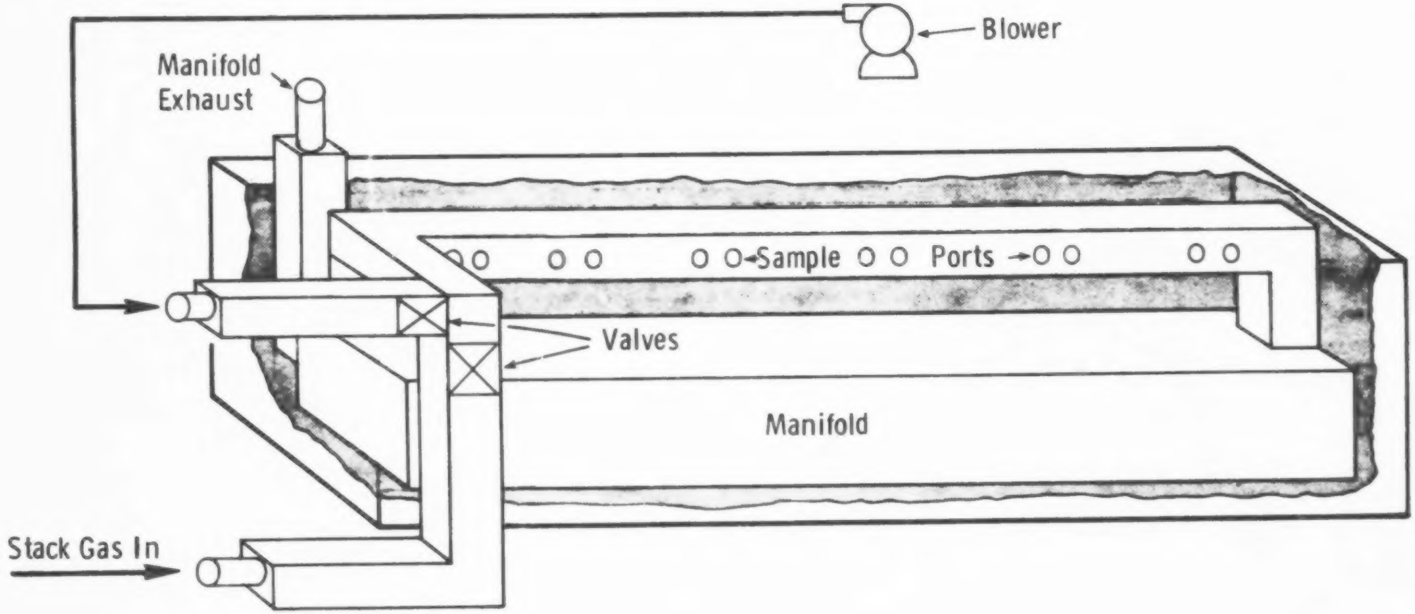
Blower
Manifold Exhaust
O O-Sample O O Ports -O O
Valves
Manifold
Stack Gas In

Figure 13. Stack Gas Delivery System and Sampling Manifold.

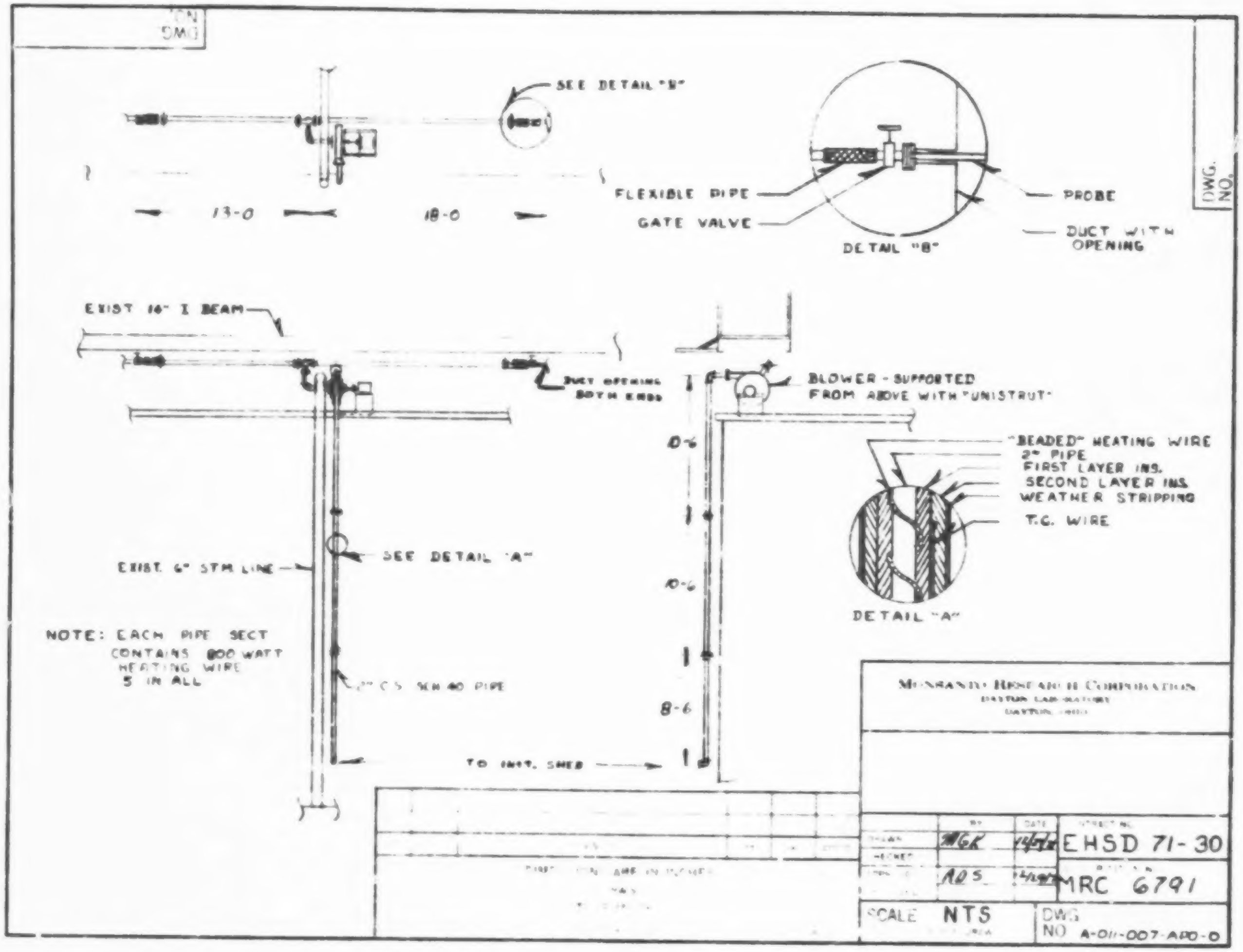
DWG NO.
SEE DETAIL "B"
13-0
18-0
FLEXIBLE PIPE
GATE VALVE
PROBE
DUCT WITH OPENING
DETAIL "B"
EXIST 14" I BEAM
DUCT OPENING BOTH ENDS
BLOWER - SUPPORTED FROM ABOVE WITH "UNISTRUT"
"BEADED" HEATING WIRE
2" PIPE
FIRST LAYER INS.
SECOND LAYER INS.
WEATHER STRIPPING
T.C. WIRE
DETAIL "A"
10-6
10-6
8-6
SEE DETAIL "A"
EXIST. 6" STM LINE
NOTE: EACH PIPE SECT CONTAINS 800 WATT HEATING WIRE 5 IN ALL
2" C.S. SCH 40 PIPE
TO INST. SHED
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
MGR
ADS
EHSD 71-30
MRC 6791
SCALE NTS
DWG NO A-011-007-APO-0

Figure 14. Main Delivery Line and Blower Locations for Power Plant Emission Study.

Reproduced from best available copy.

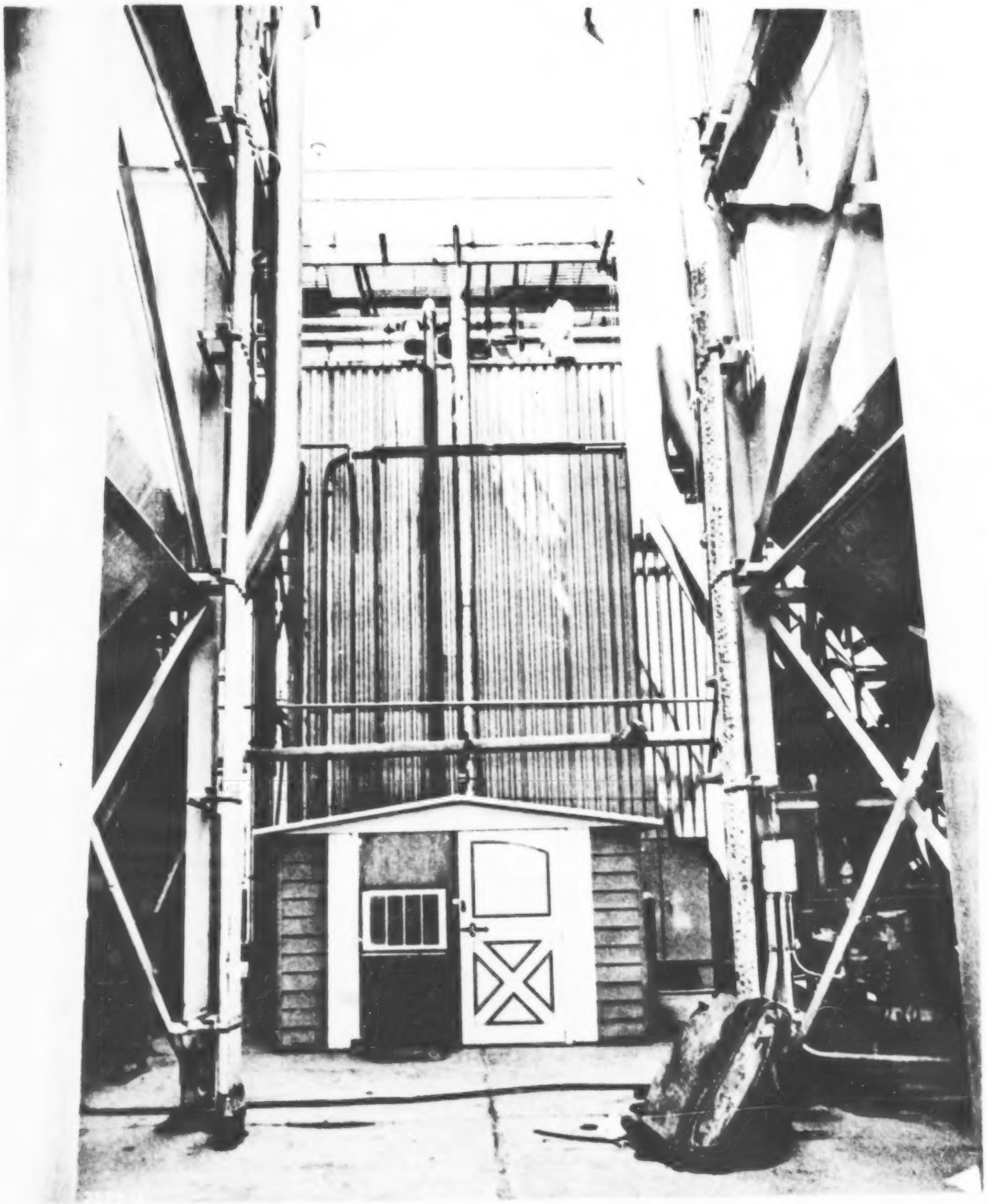

Figure 15. Power Plant Test Facility.

(3130.42 and 3131.07 Å) easily differentiated from the background emission or from nearby emission lines. A similar scan at the same wavelength with a beryllium hollow cathode lamp source showed a spectrum similar to that observed with beryllium aerosol in the arc. With clean analytical electrodes (Pt or Pt-Ir) in dry air, no emission lines are observed at the beryllium wavelengths.

When first admitting stack gas to the analytical cell operating with freshly cleaned Pt or Pt-Ir electrodes, a resolved doublet similar to that described above for beryllium appeared in the scan of the emission spectrum. However, during the repeated scans in approximately five or six minutes, the intensity of the doublet diminished and finally the doublet disappeared from the spectrum. During this time, particulate in the stack gas coated the clean electrodes, lowered the overall intensity of the arc (by visual check and by sound intensity of arc), and completely masked or destroyed any beryllium optical emission from the metal assumed to be present.

The monochromator was set to the beryllium doublet emission lines with a Be hollow cathode lamp or by arcing the beryllium aerosol. When stack gas was then admitted, a rapid decrease in intensity resulted. After attaining steady operation, a periodic fluctuation in emission at the beryllium line was observed. The increase in intensity coincided with increased particulate concentration in the stack gas. The plant blower seems to produce a cyclic emission of particulate. The cycle is approximately 40 seconds. This phenomenon was observed several times on different days of operation and a representative response pattern using a direct reading mode (non-integration) is shown in Figure 16.

A second reference monochromator and photomultiplier tube system was used to monitor fluctuations in the background signal near the beryllium doublet emission lines. By electronically subtracting out any background fluctuations it was hoped that an overall response indicative of the actual amount of beryllium present could be obtained.

The reference signal, however, was observed to fluctuate simultaneously with and at nearly the same intensity variation as the signal from the beryllium emission wavelength. No improvement was seen by adjusting the reference monochromator to a non-beryllium emission line in the stack gas spectrum. Both iron, which was present in the particulate, and platinum, the electrode material, lines were used without success. As a consequence, the measurements taken at 3131 Å could not be correlated with the Be content in the stack gas. This background phenomenon may be similar to the Mg interference reported by Webb et al (ref. 1,2).

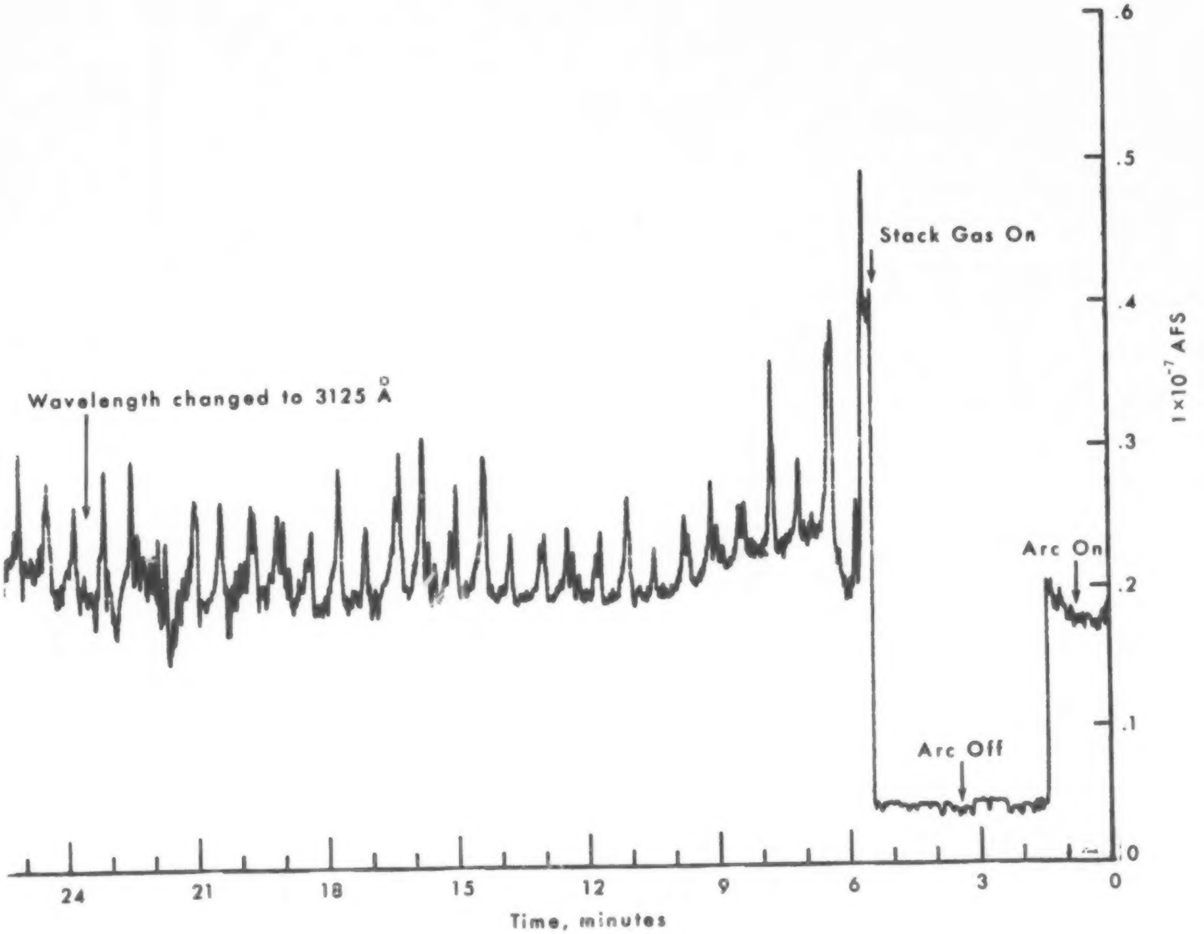

Figure 16. Typical Pattern Webb-Type Cell Emission at Be 3131 Å Line.

The two cells used in this study each had a built-in quartz window for monitoring spectral emission photoelectronically. The high energy arc ejected solid particulate (or electrode material if only air was being investigated) outwardly with velocity sufficient to impact firmly on the quartz windows. Operation for several hours left the windows completely opaque.

The problem was solved by sealing the monochromator end of the tube with a large quartz disc (held about 4 inches from the arc) and by keeping the tube at positive pressure by pumping in air at the rate of about 0.5 liters per minute. This served to dilute the stack gas somewhat (2%), but kept moisture out of the optical emission measurement system and particulate from the quartz windows.

Asbestos cannot be machined with an airtight fit, and with each disassembly for cleaning the airtight seal degrades. With the suction pump being used to pull stack gas through the MRC asbestos cell, some leakage of air and displacement of sample gas can occur. This was not a serious problem, however.

A great many difficulties were experienced with the asbestos cells. Asbestos is a satisfactory insulator when kept dry, but if wet its conductivity makes it entirely unsuitable for a cell material. A symptom which appeared regularly was high voltage arcing on the outside surface of the cell as well as on some internal surfaces. Also, the cell became physically hot through the effects of resistive heating. Purposely heating the cell may, however, prevent moisture absorption.

Particulate matter in the stack gas built up on the electrode holder surfaces and on the inner cell walls. It is likely that with extended operation the particulate matter would accumulate to such a degree that large amounts would fall randomly into the arc area.

Filter samples of the particulate were collected from the sample gas flow both after the cell (Samples #1-5) and before the cell just after the valve at the point where the sampling system joined the main line (Samples #8-13). The results are shown in Table XVI in terms of total grams particulate per cubic meter, μg of Be per cubic meter and part per million of Be in the particulate. The Be analysis was performed by atomic absorption using a Varian carbon rod atomizer. Samples 1-4 and 8-12 were sampled at the flow rate normally employed during the tests, 28 l/min. Samples 5 and 13 were sampled at 9.3 l/min and 4.7 l/min, respectively. In addition, three fritted bubblers each containing 40% HCl-8% H_2SO_4 were installed after the filters on #5 and #13. Analysis by atomic absorption showed no detection of Be in any of the bubblers

Table XVI

ANALYSIS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY OF PARTICULATE SAMPLES COLLECTED AT POWER PLANT FOR BERYLLIUM AND TOTAL PARTICULATE

Sample	Volume Sampled (m^3)	Concentration of Particulate (g/m^3)	Concentration of Be ($\mu g/m^3$)	Concentration of Be in Particulate (ppm)
1	0.246	0.508	20.6	40.5
2	0.338	0.489	18.2	37.2
3	0.285	0.396	16.7	41.9
4	0.303	0.410	10.4	25.4
5	0.283	0.305	6.4	20.8
8	0.315	0.896	45.5	50.7
9	0.290	0.655	28.8	44.0
10	0.280	0.536	17.5	32.6
11	0.283	0.666	22.6	33.9
12	0.252	0.609	34.8	57.1
13	0.312	0.581	18.5	31.8

As noted in Table XVI, a high level of particulate was being emitted from the stack. As a consequence, the deposition of fly ash contaminated the discharge cell, electrode mountings, etc., forcing a termination of the program after two weeks of intermittent operation at the power plant. Lack of time and funds precluded additional field testing.

6.1 Conclusions

At the present state-of-the-art, there is no analytical technique available for universal application as a direct, continuous, monitor of beryllium and cadmium from all types of stationary source emissions at the A.C.G.I.H. 1967-TLV levels of 0.002 mg Be/m^3 and 0.02 mg Cd/m^3 (as soluble salts and metal dust) or 0.1 mg Cd/m^3 (as CdO fume). A continuous monitoring system for beryllium in work environments was developed by Webb, et al. (ref. 1,2) based on the principle of measuring the optical emission spectrum for beryllium generated in a pulsed DC arc. The technique was used in several atomic energy projects for monitoring beryllium levels in work environments and in production facilities.

A detection level was reported by Webb et al. as 1 μg Be/m^3 and was substantiated in a modified (AC arc, rather than pulsed DC arc) in this program. No data were reported by Webb et al. for cadmium, but Webb indicated in a private communication that cadmium measurements should not be a problem. However, limited laboratory studies with cadmium aerosols and with the AC arc modification in this program show much poorer sensitivities, which were insufficient to provide detection limits equivalent to the TLV levels. Unfortuantely, no detailed study was made and data was accumulated only with the instrument conditions used for detecting beryllium. Optimization of conditions for detecting cadmium may provide the needed sensitivity. Undoubtedly, instrument conditions must be optimized for each element.

Although limited laboratory testing showed the feasibility of using the Webb type system for direct, continuous monitoring of beryllium, considerable difficulty was encountered in field tests (power plant) with a prototype, continuous monitor for measuring beryllium directly in stack effluent. However, the Webb arc emission spectroscopic system still remains the most promising approach to monitoring trace metal in work environments and in effluent from stationary sources. The advantages are: (a) direct, real time, continuous measurements down to low trace levels (1 μg/Be/m^3); (b) specificity; (c) moderate volume flow rate (up to 40 l/min); and (d) relatively simple low weight instrument package. Lower detection limits <<1 μg Be/m^3 can be obtained by integrating the emission signal for 30-60 seconds, resulting in sampling and analysis times of approximately 30-90 seconds. For beryllium, the analytical working range by direct measurement without signal integration is 1 μg - 200 μg Be/m³. Problems to be solved include: (a) fouling of the electrodes and cell with particulate deposits when monitoring stack effluents having high loadings of refractory (silicate) particulate, and (b) absorption of moisture and other stack gases by the asbestos cell resulting in a breakdown of electrical insulation.

With minor design changes, the Webb type cell system could be used to monitor beryllium directly from emission sources having relatively low loadings of particulate. Applications include beryllium machining operations and beryllium ore processing operations.

For stationary emission sources, yielding relatively high loadings of refractory silicate particulate, a much hotter vaporization system other than the Webb cell design is needed. In the Webb cell, the relatively small arc zone serves to vaporize the particulate and to induce optical emission spectra but does not have sufficient energy to accomplish both simultaneously and efficiently. Solutions to this problem would involve either the addition of a vaporizing system immediately prior to the analytical arc discharge or the use of a hotter analytical discharge system. In the former case, an auxiliary arc could be used to vaporize the particulate prior to the analytical arc. With the latter approach, a hotter excitation system - radio-frequency induced plasma or Shumaker arc oven - would be used.

The problem of providing enough energy to vaporize sample and to excite analyte to optical emission is the major deficiency when applying the Webb arc system to source emissions containing relatively high loadings of particulate. Dr. R. Mavrodineanu (ref. 18) suggested that an arc source developed by Shumaker (ref. 19) for high temperature (in excess of 13,000°K) gas studies may be applied to solve the problem.

The Shumaker arc chamber is a tube-shaped device with quartz windows in both ends. Hollow graphite electrodes are placed near the ends where argon gas is added to keep them in an inert atmosphere and to keep the quartz windows clean. Sample gas enters through the middle of the side of the tube, and it is exhausted via ports one-fourth of the total length from either end. The arc length is 10 cm and 3/16-in. diameter and is viewed through the hollow graphite electrodes. The device is water cooled.

In operation, a very high current DC arc is struck between the electrodes. Argon gas enters near the ends and sheaths the electrodes in an inert gas atmosphere to prevent their erosion. Sample enters the oven and is exhausted along with the argon sheath gas. Spectroscopic emission passing through the quartz windows is monitored with the usual instrumentation.

Advantages of the Shumaker arc chamber are its durable electrodes requiring infrequent adjustment, its extremely high excitation energies, and its clean-window, low maintenance design. Disadvantages are the high power (25 kw) necessary for operation and the need to supply an inert gas (argon) during operation. Also, sample flow rates and potential deposition problem need to be evaluated. The device is available commercially (TAFA Division, Humphreys Corporation, New Hampshire).

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APPENDIX I

SAMPLING SYSTEM CONSIDERATIONS AND DESIGN

1. INTRODUCTION

In the beryllium-cadmium monitoring system, as in any source emissions monitoring system, sampling must be accomplished in a manner to assure that a representative sample is delivered to the detector. Design of the sample probe and sample transport subsystems must take into account the multiphase properties of the emissions from a number of major industrial sources of beryllium and cadmium.

2. TRANSPORT OF PARTICULATE THROUGH A SAMPLING TRAIN

Previous experience in sampling and collection of particulate from stationary sources has centered on the use of filter/ liquid impinger trains using the EPA sampling system. Concern exists regarding the efficiency of the collection systems when collecting even relatively nonvolatile particulate. The high throughput of stack gases, the presence of moisture and reactive gases (O_2, HCl, NO_x, SO_x, etc.), and the long sampling times and lengthy exposure of high surface-to-volume ratio particles may adversely affect the volatilization of substances contained on the filter which are normally considered nonvolatile.

During field sampling of emissions from a beryllium machining plant using a typical EPA sampling train, a relatively uniform distribution of beryllium throughout the sampling train was observed (ref. 1). Little particulate was obtained on the filter with a majority found in either the sampling probe or in the impingers. Since the distribution of beryllium in the impingers did not decrease progressively when a number of impingers were arranged in sequence, slippage of beryllium was apparent. No specific reason can be given for this behavior although slippage of submicron particles, formation of relatively volatile organometallic compounds, and volatilization of hydrated BeO may be contributing factors. Deposition in the probe may result from electrostatic effects of the probe walls on the very small particles.

Although little data are available that show transport of BeO or other metal oxides at low to moderate temperature (i.e., <200°C), volatilization of B_2O_3 (ref. 2), BeO (ref. 3,4) and Cr_2O_3 (ref. 5) has been reported at temperatures in the range of 1000-1400°C in the presence of water and in an oxidizing atmosphere. The mechanism for the vaporization promoting effect of water has not been completely established; however, in the case of Be and B the formation of volatile hydrates has been proposed (ref. 2,4). In the case of Cr_2O_3, moisture may change the activation energy and serve as a promoter for the surface oxidation of Cr_2O_3 to the more volatile CrO_3 (ref. 5).

Losses of the more volatile mercuric compounds can occur as vaporization of the specific compound or through a disproportionation reaction in which the very volatile elemental mercury is formed.

Volatilization of lead monoxide occurs at approximately 530°C and some indications of vaporization have been reported at room temperature (ref. 6). The vaporization of lead chloride occurs at 225°C in a stream of HCl and the volatilization of lead sulfide vaporization by currents of combustion gases in metallurgical furnaces is reported (ref. 5).

Losses of elemental nickel can occur as volatile nickel carbonyl. Nickel carbonyl can be formed in significant amounts (1 ppm to >1000 ppm) at 25°C, when the concentration of carbon monoxide ranges from 100 ppm to 3 Mole % in presence of finely divided nickel (ref. 7). Gases containing some carbon monoxide were found to contain nickel carbonyl after passing through nickel-alloyed pipes (ref. 8).

Information on the transport mechanisms of metallic elements and their compounds is lacking, particularly with respect to collecting submicron particulates containing microgram quantities of the elements sought. The problem can be compounded by the need for processing large volumes of stack gas.

Since beryllium emissions can be transported throughout an EPA-approved sampling train, the use of filters and impinger systems is not desirable for use in the Be/Cd monitoring systems. As stated earlier, a sampling and transport system delivering vapor and aerosol directly to the detector was selected for this study.

3. SAMPLE INTAKE PHENOMENA

To ensure that the sample drawn through the sample tube is representative of the aerosol in the main gas stream, the following conditions must be met:

(1) The tube must be aligned in a direction parallel to flow with mouth facing upstream, especially when particles >2 μm are present.

(2) The velocity of gas in the sample tube must equal the velocity of the main gas stream (isokinetic).

(3) The walls of the sample probe must be very thin (unobstructed flow).

Departures from these criteria result in nonrepresentative sampling. The most difficult criterion to meet is isokinetic sampling, and has been the subject of numerous technical papers.

The Environmental Protection Agency (EPA) requires that all particulate sampling systems used for emission controls be isokinetic. Under certain conditions, however, representative sampling can be achieved without strict adherence to isokinetic conditions. When the size of the particles becomes exceedingly small, the aerosol behaves as an ideal gas, and representative samples can be obtained without isokinetic conditions. Figure 1 (ref. 9,10) shows the sampling efficiency obtained for various particle sizes with a sample probe aligned parallel to main stream flow. It is apparent that the efficiency of collection is nearly unity for all sampling velocities for particles below 4 micron in diameter. Figure 2 (ref. 10) shows the effect of sampling angle upon particle sampling efficiency. The efficiencies of collection approach unity for sampling angles <45°. For particle sizes <4μ collected at a sampling angle <45° the sampling error can be neglected.

The preliminary field testing (Section 4.0) indicated that (1) all of the particulate sampled from the power plant after the electrostatic precipitator had diameters below 7 microns, and (2) that the beryllium and cadmium from the incinerator effluent, while distributed between the stages of a cascade impactor, showed a maximum concentration in the particle size range 0.74-1.9μ for Be and 0.24-1.1μ for Cd. These findings would support the use of a non-isokinetic sampling procedure. Since, however, the incinerator employed a wet scrubber and large water droplets containing Be and Cd are released to the atmosphere, isokinetic sampling is recommended. Proprietary information furnished to MRC by a beryllium manufacturer and refinery indicated that the beryllium distribution in stack effluents was binodal in nature with maximas occurring at aerodynamic particle sizes (water droplets) greater than 30μ and at size ranges from 3.3 down to 0.3μ, depending on the emission source.

4. PARTICLE DEPOSITION ON TUBE WALLS

Particles can deposit on the walls of delivery tubes by either diffusion or gravitational settling. The relative importance of these two phenomena is a function of particle size, flow rate, tube diameter and tube length. The magnitude of these deposition rates or efficiencies is given below.

4.1 Particle Loss by Gravitational Settling

When particles are transported in a horizontal tube, the particles within the gas stream tend to settle due to the gravitational force acting on them. For a circular tube with laminar flow, Fuchs (ref. 11) gives the following equation for calculating collection efficiencies:

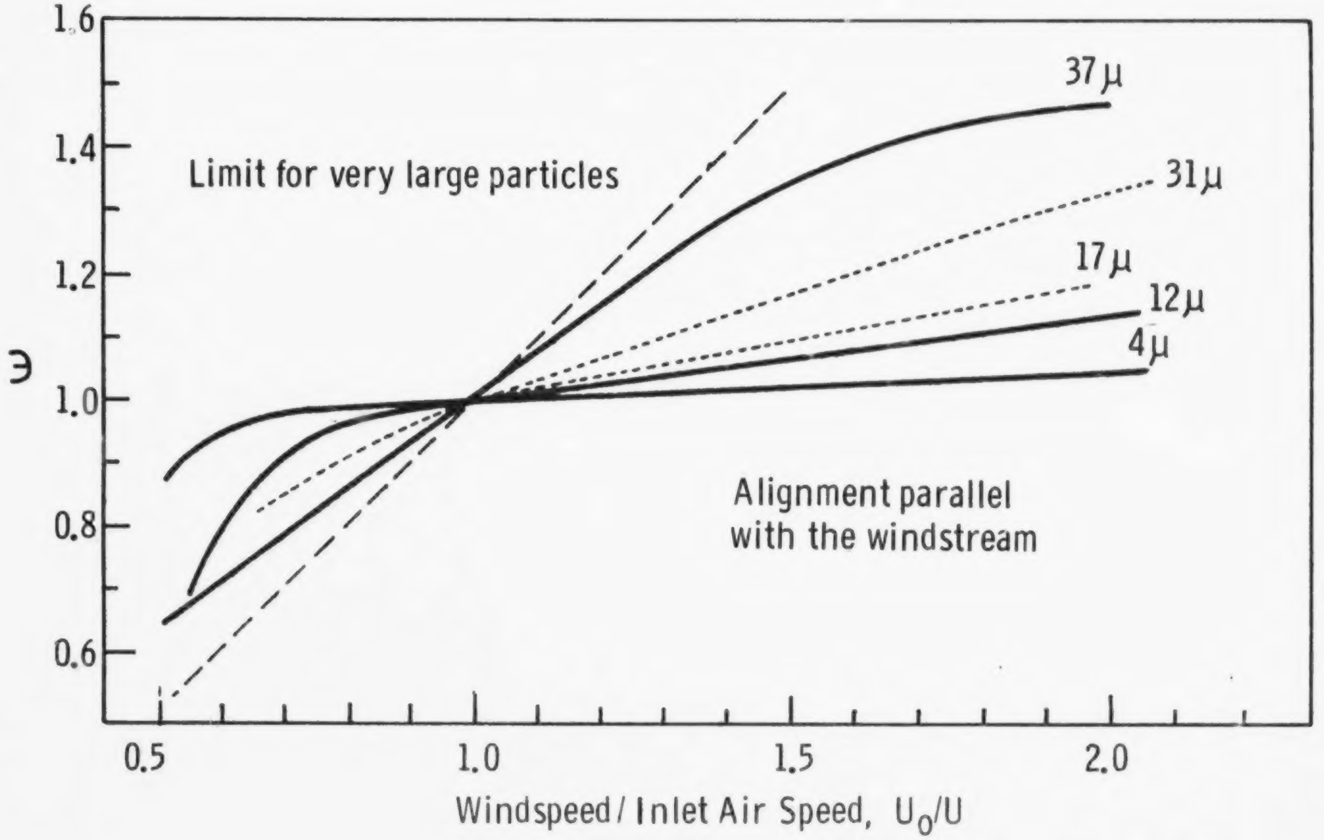

Figure 1. Sampling Efficiency and the Ratio of Flow Rates Inside and Outside a Sampling Tube.

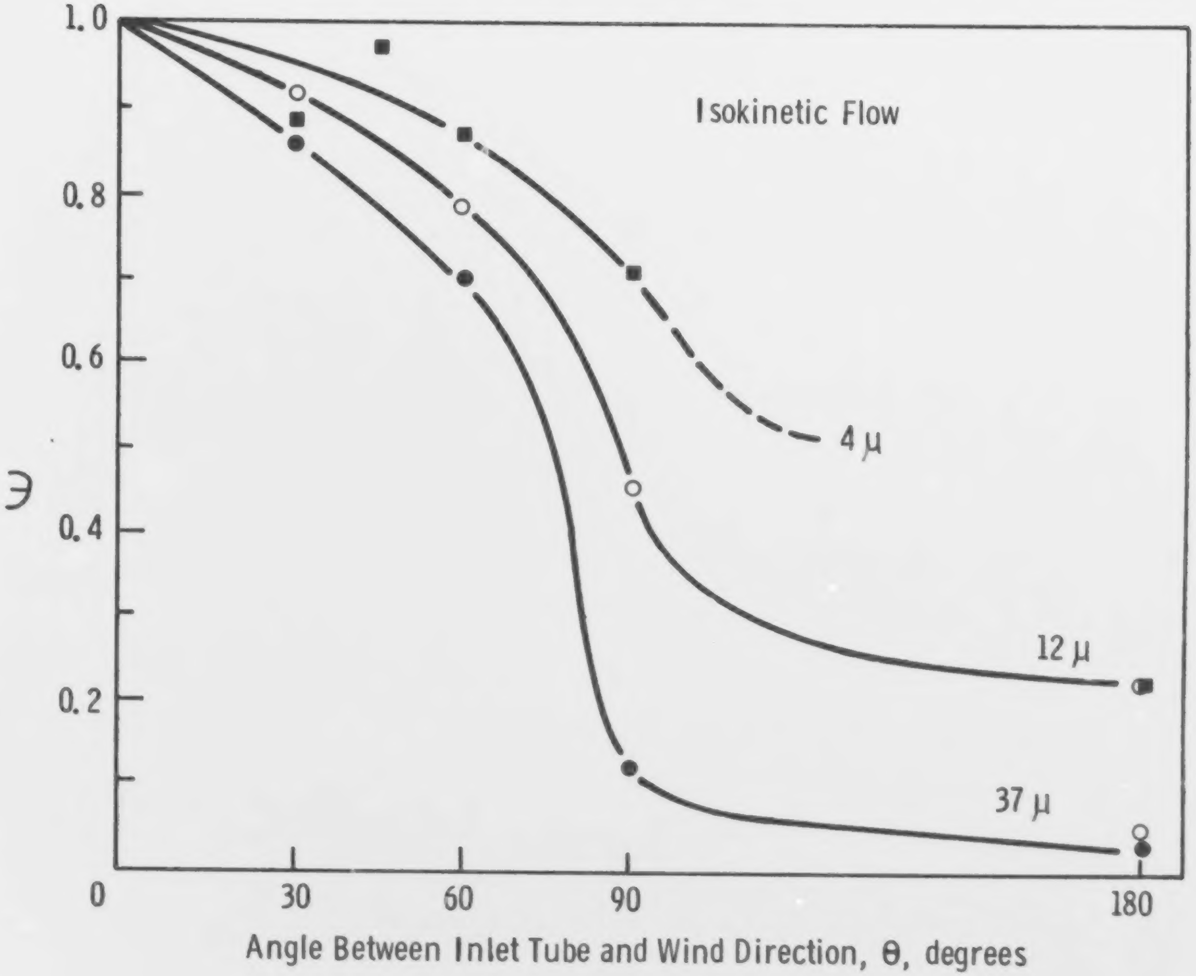

Figure 2. Sampling Efficiency and the Angle Between the Axis of the Sampling Tube and the Flow Direction.

$$= \frac{2}{\pi} \left(2\mu\sqrt{1-\mu^{2/3}} + \arcsin \mu^{1/3} - \mu^{1/3}\sqrt{1-\mu^{2/3}}\right) \qquad (1)$$

where

$$\mu = \frac{3V_sL}{8\ R\overline{U}} = \text{ a dimensionless parameter,}$$

and L = tube length
R = tube radius
V_s = particle velocity
$\overline{U}$ = mean horizontal velocity

Figure 3 is a plot of particle collection efficiency in a horizontal tube with laminar flow as a function of the dimensionless parameter μ.

Early plans on the project included an rf excitation source for the Be/Cd monitor at a sample flow rate of about 300 cc/min. To determine the importance of deposition, the following assumptions have been made.

(1) Flow rate - 5 cc/sec

(2) Tube length in horizontal position - 100 cm

(3) Tube diameter - 2 cm

(4) Setting velocities are obtained from relaxation time parameters given in reference 12.

The value μ can be calculated as follows:

$$\mu = \frac{3\pi gTRL}{8\ \text{Vol}} \qquad \text{where } gT = V_s \text{, and } \frac{\pi R}{\text{Vol}} = \frac{1}{R\overline{U}}$$

and g = acceleration of gravity
T = relaxation time
Vol = volume flow rate

Particle Diameter (μ)	Relaxation Time Constant T (sec)	Parameter In Eq. (1) (μ)	Collection Efficiencies (F)
20	1.23×10^{-3}	28.4	1.00
10	3.08×10^{-4}	7.11	1.00
4	5.03×10^{-5}	1.16	1.00
2	1.31×10^{-5}	0.302	0.44
1	3.54×10^{-6}	0.082	0.15
0.4	6.87×10^{-7}	0.016	0.03
0.2	2.28×10^{-7}	0.005	0.01
0.1	8.81×10^{-8}	0.002	0.004

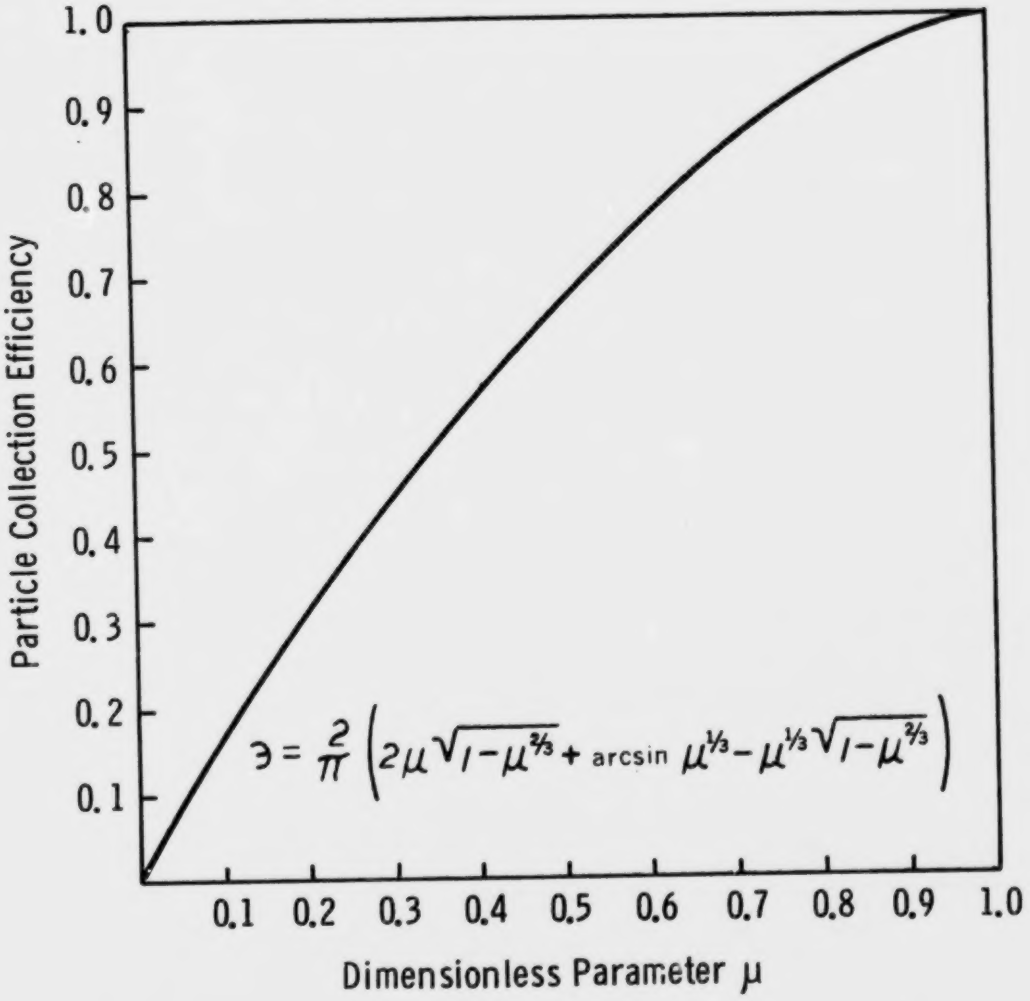

Figure 3. Particle Collection Efficiency in Horizontal Tube with Laminar Flow.

Thus for a 2-cm diameter tube having a 1.0 meter horizontal run and delivering 5 cc/sec, all particles greater than 4.0 microns will be deposited and half of the particles ∿2 microns will be deposited.

Changing the the tube diameter from 2 cm to 2 mm has the following effect on collection efficiency:

Particle Diameter (μ)	Relaxation Time Comstan TL (sec)	Parameter in Eq. (1) (μ)	Collection Efficiency (F)
20	1.23×10^{-3}	2.84	1.00
10	3.08×10^{-4}	0.771	0.85
4	$5.03 \times 10^{-}$	0.116	0.18
2	1.31×10^{-5}	0.030	0.05
1	3.54×10^{-6}	0.008	0.016
0.4	6.87×10^{-7}	0.002	0.003
0.2	2.28×10^{-7}	<0.001	0.001
0.1	8.81×10^{-8}	<0.001	<0.001

Thus it appears that the delivery line should be kept as small as possible to prevent particle deposition due to gravity. With a 2 mm tube diameter and a 300 cc/min. flow rate, the flow is well into the laminar flow regime.

These calculations were conducted assuming a flow rate of 300 cc/min to the detector. At the higher flow rates actually employed on the program, the degree of deposition would be even smaller than that calculated above since the increased linear velocity would decrease the value of the dimensionless parameter μ. In a 2-mm tube, however, a total volume flow rate in excess of 4 liters/minute would result in turbulent flow conditions which would not permit use of the laminar flow assumption.

4.2 Particle Loss by Diffusion to Walls

When an aerosol is flowing in a tube in laminar flow, particles can migrate to the wall by diffusion where they are removed from the gas stream. Gormley and Kennedy (ref. 13) give a formula for calculating collection efficiencies in a tube due to particle diffusion.

$$\ni = 2.56\mu^{2/3} - 1.2\mu - 0.177\mu^{4/3} \qquad (2)$$

where μ is the dimensionless group DL/R^2U, where D = diffusion coefficient.

Substituting $Vol = \pi R^2 U$ into the expression for μ, we find that

$$\mu = \frac{\pi DL}{Vol}$$

Values of D are given in reference 12.

Particle Diameter (μ)	Diffusion Coefficient (cm^2/sec)
20	1.38×10^{-8}
10	2.38×10^{-8}
4	6.10×10^{-8}
2	1.27×10^{-7}
1	2.74×10^{-7}
0.4	8.32×10^{-7}
0.2	2.21×10^{-6}

Taking 300 cc/min. as our flow rate, and 5 meters as our delivery tube length, the following collection efficiencies will occur as a result of particle diffusion.

Particle Diameter (μ)	Dimensionless Parameters	Collection Efficiency
20	4.3×10^{-7}	0
10	7.5×10^{-6}	0
4	1.9×10^{-5}	0
2	4.0×10^{-5}	0
1	8.7×10^{-5}	0
0.4	2.6×10^{-4}	∿0.01
0.2	7.0×10^{-4}	∿0.02

For our purposes, the loss of particulate matter by diffusion is negligible. This is true for any tube diameter, a somewhat surprising relationship. An increase in volume flow rate would tend to minimize diffusional wall losses of particulate.

A recent paper by Yamada and Charlson (ref. 14) discusses the serious measurement errors that can result by diffusive loss of gaseous pollutants to inlet line walls. The fact that the diffusion coefficients of particulate matter (1-10μ) are a factor of about 10^6 lower than gaseous species accounts for the negligible loss of sampled particulate by this mechanism.

5. RECOMMENDED SAMPLING SYSTEM

Based on the considerations presented above, a sampling system design approach was selected which included isokinetic sampling of a primary sample stream at flow rates of about

2 cu.ft/min, followed by secondary sampling of this primary stream to isolate a constant flow sample for delivery to the analytical instrumentation. Two sampling systems were designed and/or used on the program. The first system was designed and packaged to supply a 300 cc/min flow to the rf induced emission detection instrument. The second system was that employed in preliminary field testing of the AC discharge arc emission approach at a neighboring power plant. These systems are described in the following subsections.

5.1 RF Induced Emission Be/Cd Monitor Sampling System Design

The design of the Be/Cd monitor sampling system was based on the following requirements:

(1) The Be/Cd excitation by r-f requires a constant flow rate of sample gas.

(2) The Be/Cd excitation chamber requires metered amounts of dilution gas and purge gas.

(3) The sampling system should minimize particle deposition resulting from gravitation.

To meet these requirements, the sampling system was designed in two stages. The stack effluent is first obtained via an isokinetic sampler similar to that employed in Method 5. This effluent gas flow is then sampled in a second stage (2-mm diameter tube) to extract a subsample at constant volumetric flow which is delivered to the radiofrequency induced excitation chamber. Some sacrifice in isokinetic conditions is inherent in the second-stage sampling, but for power plant, incinerator and metallurgical operations with efficient electrostatic precipitators or baghouse control equipment, this may not be too serious a problem since particle sizes may be largely below 4μ. As mentioned previously, wet-scrubber controlled processes can result in metal emissions associated with large (>30μ) water droplets. In this case it may be feasible to sample at elevated temperature, thereby vaporizing the droplets upstream of the secondary sampling stage.

5.1.1 Isokinetic Sampling System

Figure 4 shows a schematic representation of a typical isokinetic sampling train. It consists of a dual purpose sample probe, a series of impingers, a gas pump, a wet test meter and associated pressure gauges, thermometers, valves and tubing. Figure 5 shows a schematic representation of the isokinetic sampling control console.

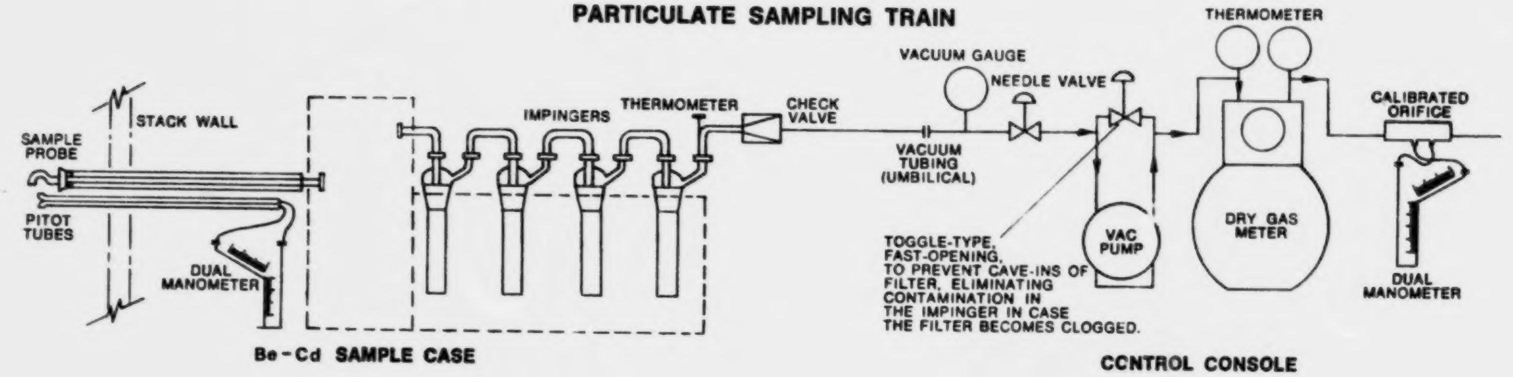
PARTICULATE SAMPLING TRAIN
SAMPLE PROBE
PITOT TUBES
STACK WALL
DUAL MANOMETER
Be-Cd SAMPLE CASE
IMPINGERS
THERMOMETER
CHECK VALVE
VACUUM TUBING (UMBILICAL)
VACUUM GAUGE
NEEDLE VALVE
TOGGLE-TYPE, FAST-OPENING, TO PREVENT CAVE-INS OF FILTER, ELIMINATING CONTAMINATION IN THE IMPINGER IN CASE THE FILTER BECOMES CLOGGED.
VAC PUMP
THERMOMETER
DRY GAS METER
CALIBRATED ORIFICE
DUAL MANOMETER
CCNTROL CONSOLE

Figure 4. Schematic Representation of Isokinetic Sampling Train.

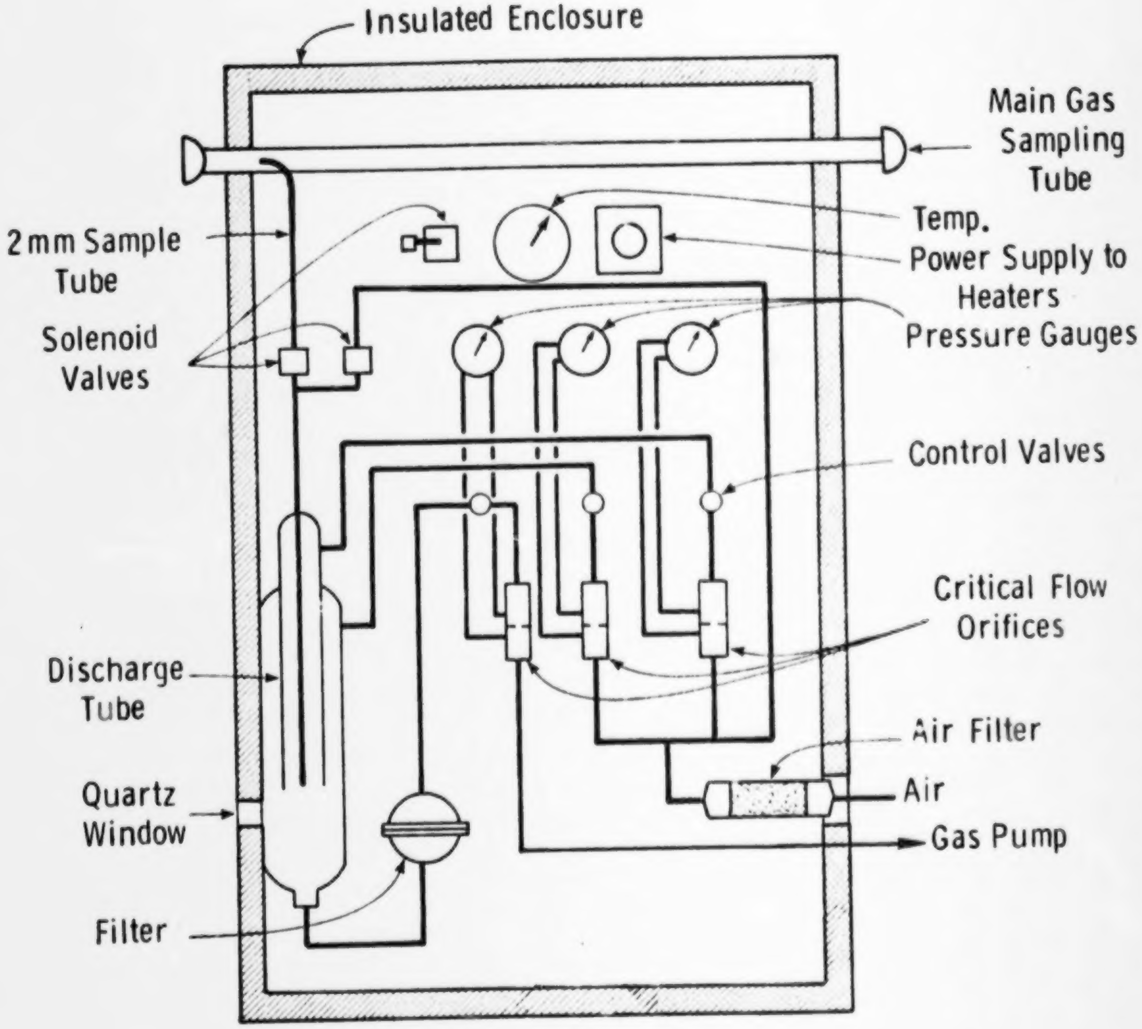
Insulated Enclosure
Main Gas Sampling Tube
2mm Sample Tube
Temp.
Power Supply to Heaters
Solenoid Valves
Pressure Gauges
Control Valves
Critical Flow Orifices
Discharge Tube
Air Filter
Air
Quartz Window
Gas Pump
Filter

Figure 5. Be/Cd Sample Compartment.

5.1.2 Be/Cd Sampling Compartment

The Be/Cd sampling compartment (omitted in Figure 4) is shown in Figure 6. The concept of this system is to sample a sub-sample at constant volumetric flow rate from the isokinetic sample delivery tube. The sub-sample will, of necessity, be taken non-isokinetically since a constant volume of about 300 cc/min. is required. In a truly isokinetic sampling system, the sampling rate varies as the velocity of gases in the stack varies. Furthermore, the extremely low sampling rate of 300 cc/min. would mean that the sampling tube diameter should be about 0.5 mm to approach flow velocities normally obtained in commercial stacks.

Although the design does not include isokinetic sampling in the Be/Cd sample tube, we believe the sample will still be representative. This belief is based upon the expectation that most particulate discharges will have some type of collection system, thereby effectively removing all but the finer particles. As discussed previously, the adverse effects of non-isokinetic sampling decrease with decreasing particle sizes.

Once the sample enters the Be/Cd sampling tube, every precaution is taken to prevent particle deposition. Horizontal runs are kept to a minimum, flow velocities are kept as high as possible, all lines are maintained above the dew point temperature of the sample gas and obstructions to the flow are held to a minimum.

As shown in Figure 3, the flow rates of the dilution gas, purge gas and total flow are measured by critical flow orifices and controlled by fine-metering control valves. The pressure drop through the orifices are measured by sensitive pressure gauges.

A simple gas pump is used to deliver the sample gas, purge gas and elution gas. The gases will be discharged to a suitable vent.

The entire Be/Cd sampling system is housed in a temperature-controlled heated enclosure. A quartz window in the side of the enclosure provides a means for observing the discharge glow. Solenoid valves, operated by a single relay, admit either sample gas or air to the excitation chamber.

5.2 Power Plant Facility for Testing of the AC Arc Discharge Emission Detector

Late in this program preliminary field testing of the AC arc discharge emission detection instrumentation was conducted using a facility employed previously at a power plant (ref. 15).

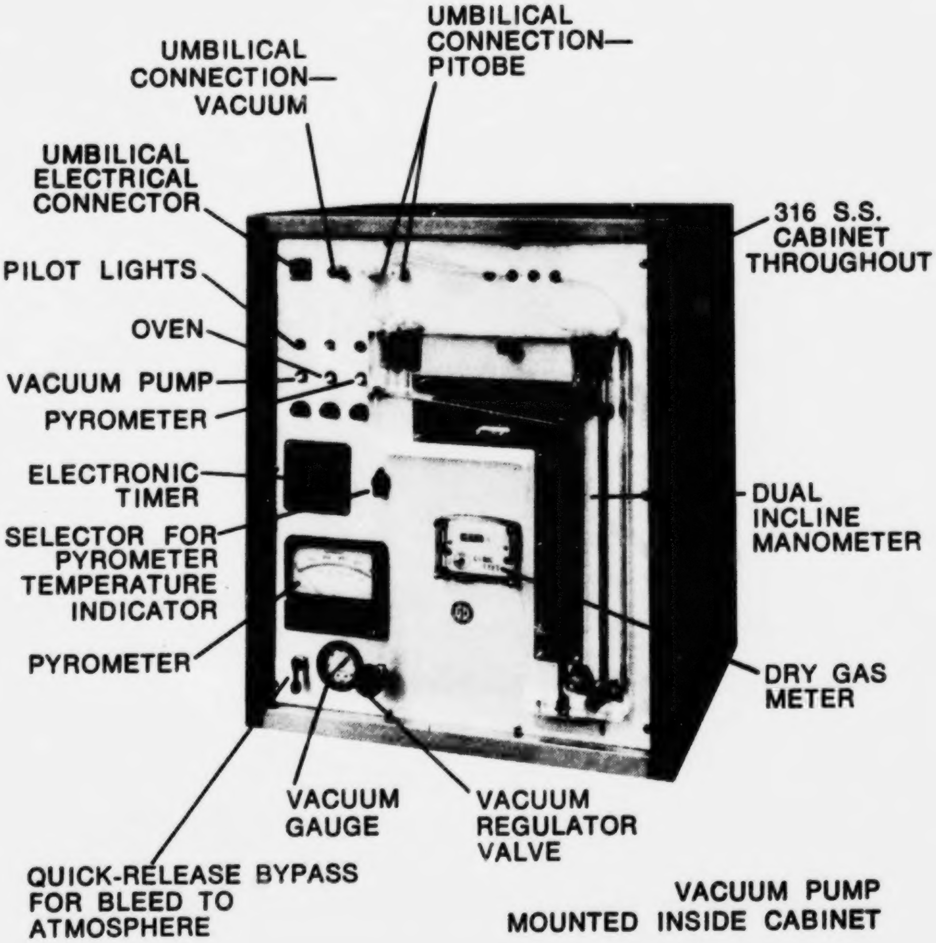
UMBILICAL CONNECTION— PITOBE
UMBILICAL CONNECTION— VACUUM
UMBILICAL ELECTRICAL CONNECTOR
PILOT LIGHTS
OVEN
VACUUM PUMP
PYROMETER
ELECTRONIC TIMER
SELECTOR FOR PYROMETER TEMPERATURE INDICATOR
PYROMETER
316 S.S. CABINET THROUGHOUT
DUAL INCLINE MANOMETER
DRY GAS METER
VACUUM GAUGE
VACUUM REGULATOR VALVE
QUICK-RELEASE BYPASS FOR BLEED TO ATMOSPHERE
VACUUM PUMP MOUNTED INSIDE CABINET

Figure 6. Isokinetic Sampling Control Console.

Figure 7 is a drawing of the stack gas delivery system and sampling manifold employed in the field test facility. Figure 8 shows the top front and side views of the delivery line and blower installation used to draw samples from ducting before the I.D. fans from either of two boilers. The two sample lines joined before entering the high pressure blower, located atop the elevator shaft. The blower was capable of delivering 100 cfm of 300°F gas at an increase of 22-inches W.G. Since the sample points were at a negative 15-inch W.G., the effective pressure of the gas downstream of the blower was 7-inches W.G. The 2-inch diameter Schedule 40 carbon steel delivery line carried the sample from the blower down to the power plant roof, about 32 feet below. All sections of the delivery line and blower were heated and insulated. The entire system was weatherproofed.

A 10-ft x 14-ft prefabricated steel shed is installed on the roof. Figure 9 is a picture of the power plant test facility showing the blower, delivery line and the exterior of the shed with a 23,000 Btu air conditioner installed in one of the doors.

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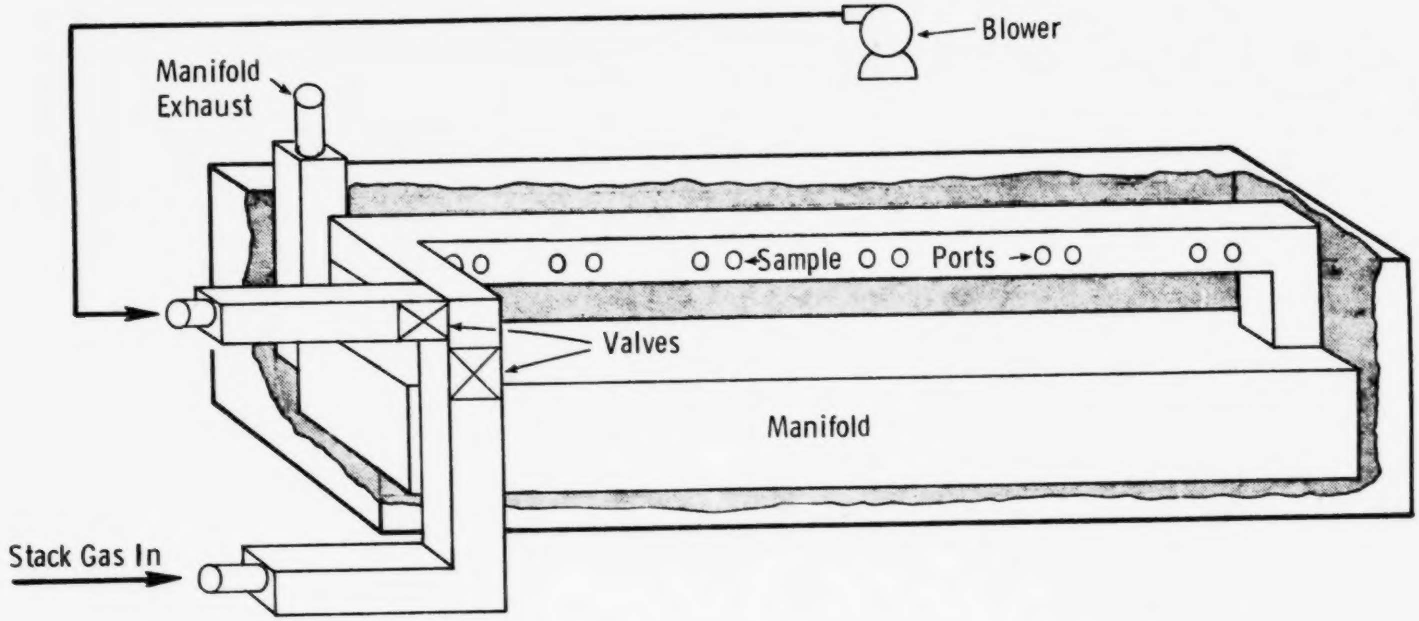
Blower
Manifold Exhaust
O O←Sample O O Ports →O O
Valves
Manifold
Stack Gas In

Figure 7. Stack Gas Delivery System and Sampling Manifold.

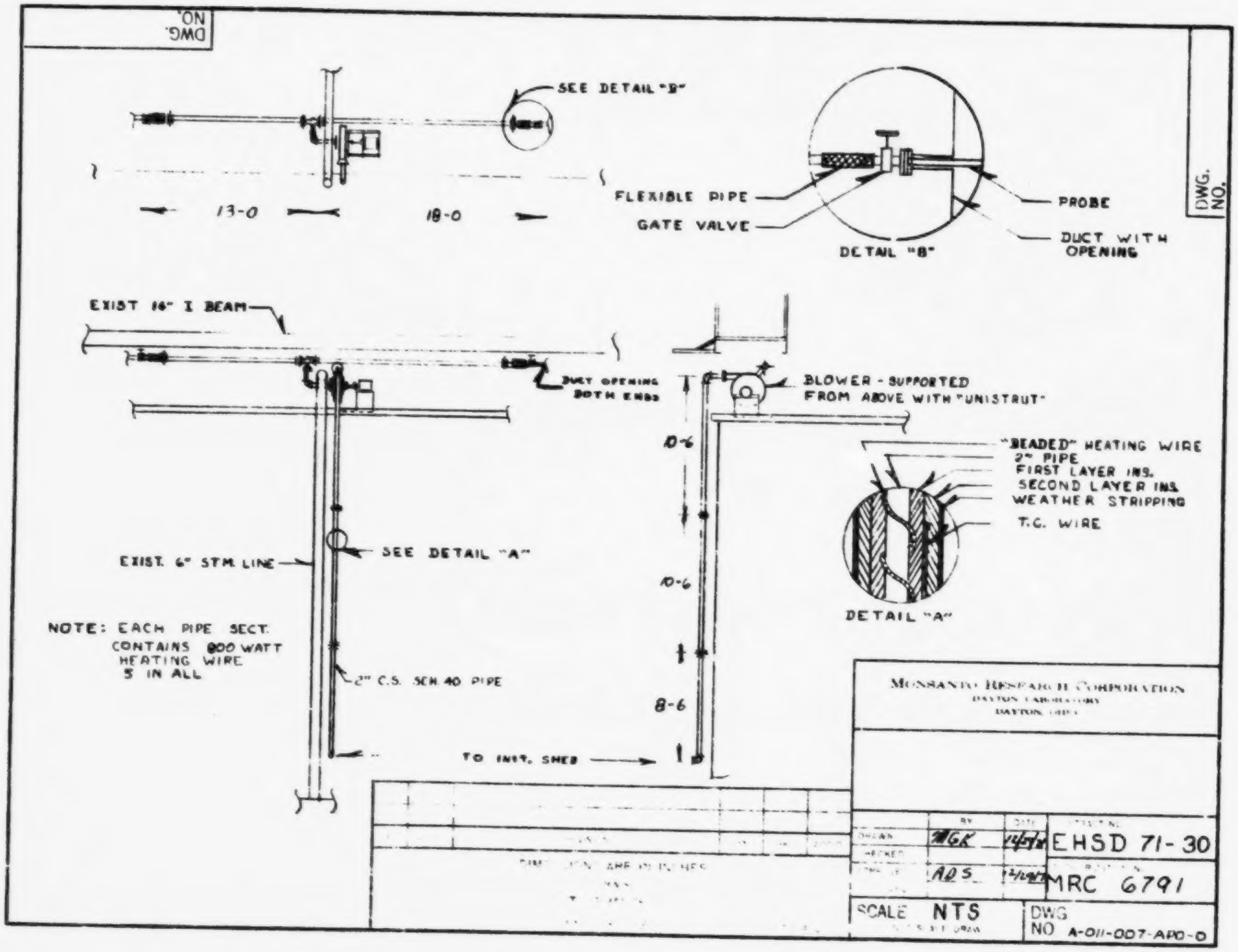
DWG. NO.
SEE DETAIL "B"
FLEXIBLE PIPE
GATE VALVE
PROBE
DUCT WITH OPENING
DETAIL "B"
13-0
18-0
EXIST 16" I BEAM
DUCT OPENING BOTH ENDS
BLOWER - SUPPORTED FROM ABOVE WITH "UNISTRUT"
"BEADED" HEATING WIRE
2" PIPE
FIRST LAYER INS.
SECOND LAYER INS.
WEATHER STRIPPING
T.C. WIRE
DETAIL "A"
SEE DETAIL "A"
EXIST. 6" STM. LINE
NOTE: EACH PIPE SECT. CONTAINS 800 WATT HEATING WIRE 5 IN ALL
2" C.S. SCH. 40 PIPE
10-6
10-6
8-6
TO INST. SHED
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
DRAWN
CHECKED
BY
DATE
WGK
ADS
EHSD 71-30
MRC 6791
SCALE NTS
DWG NO A-011-007-APO-0
DIMENSIONS ARE IN INCHES

Figure 8. Main Delivery Line and Blower Locations for Power Plant Stack Emission Study.

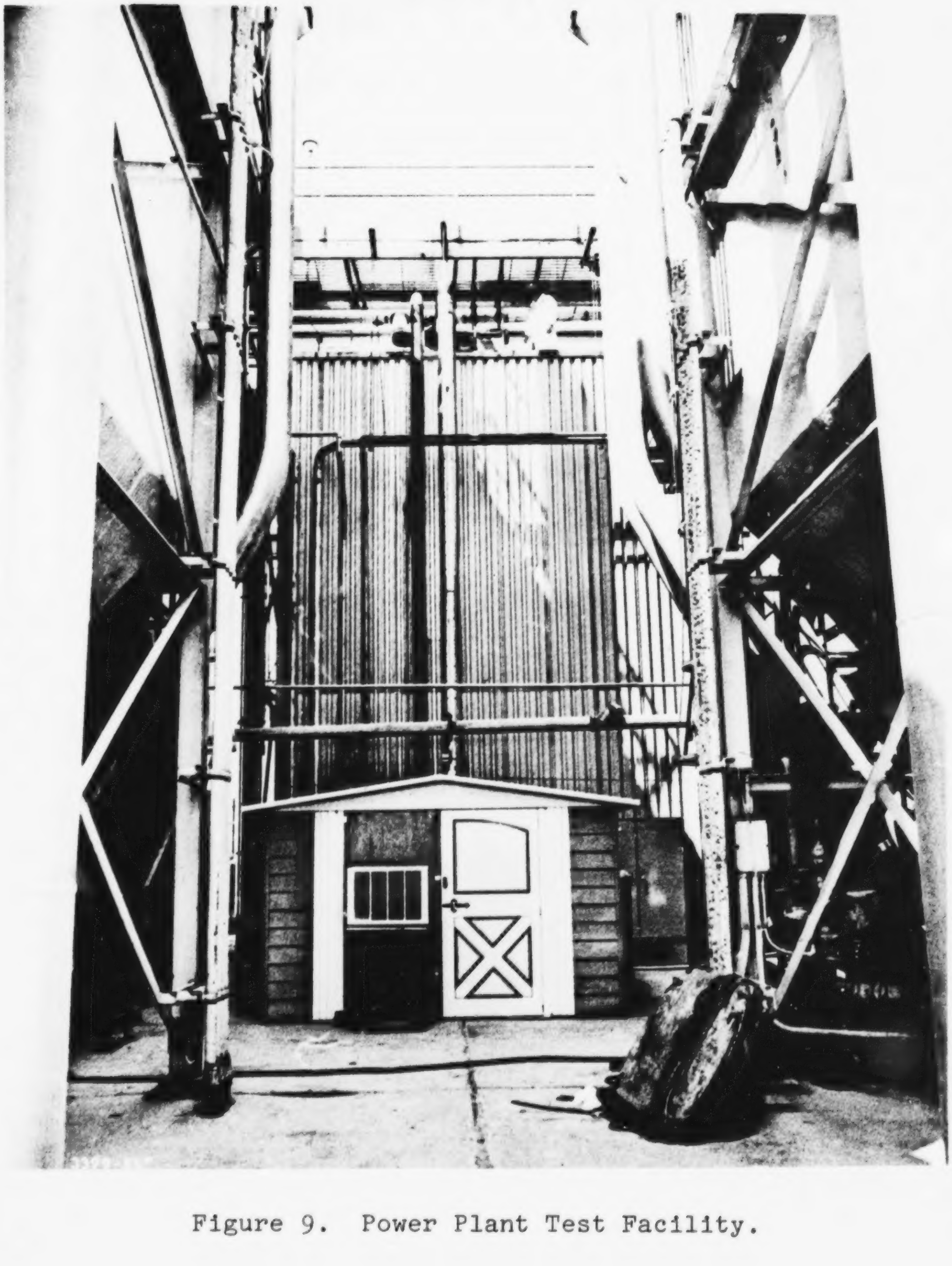

Figure 9. Power Plant Test Facility.

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APPENDIX II

BRIEFING DOCUMENT - ANALYTICAL TECHNIQUES FOR BERYLLIUM AND CADMIUM

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ANALYTICAL TECHNOLOGY FOR CONTINUOUS MONITORING OF STATIONARY SOURCE EMISSIONS FOR BERYLLIUM AND CADMIUM

1. INTRODUCTION

The chemical and physical properties of beryllium and cadmium and their compounds, which influence the selection of methods for quantitative analyses, differ considerably between each element. Analytical techniques that can be applied to one element and its compounds cannot necessarily be applied to the other.

Fundamental differences in atomic structure and nature of compound formation for each element restrict application of certain analytical techniques based on nuclear or atomic properties to individual elements and their compounds and do not allow application for analyses of both elements by the same technique. Analytical techniques for trace analyses based on x-ray emission of characteristic radiation for cadmium (atomic number 48) cannot be applied to beryllium (atomic number 4). Conversely, photoneutron excitation techniques which can be applied to beryllium cannot be used with cadmium.

Spectrographic methods have been devised for trace analyses of both elements, beryllium and cadmium. However, differences in volatility and attendant response factors influence operating conditions for attaining maximum sensitivities for each element.

In selecting a continuous monitoring device for both beryllium and cadmium emissions from stationary sources, there are two options. Two analytical methods, based on measuring different properties and requiring different measuring systems and optimized for maximum response can be incorporated into one monitor. However, the more ideal alternative would be to select one measuring system which is highly selective and responsive to both elements.

The following briefing document was prepared to show potential methods of analysis, some of the limitations of the techniques, possible problems in applying the procedures, and recommendations for the most acceptable approaches. Emphasis was placed on five prime factors, analytical reliability (accuracy and precision), selectivity, sensitivity, a continuous operation mode, and speed. Other factors (personnel, apparatus, installation, and maintenance requirements and costs) although important, can be controlled by proper hardware design and are emphasized to a lesser degree.

Continuous monitoring can be defined in a very restrictive sense as being only real-time measurement with no sample pretreatment. However, the present technology in abatement control and detection systems may permit only an approximation of continuous sampling and measuring.

Many manual techniques currently used for monitoring trace metal emissions, while meeting criteria of analytical reliability, selectivity and sensitivity, require moderate to lengthy time periods for sample pretreatment and are not considered or evaluated in this document. An analytical method was not eliminated simply based on need for preliminary pretreatment, but was screened based on whether the treatment, including chemical reactions, could be performed at the site, unattended, and within a total measuring time of five to ten minutes.

Since some of the chemical and physical properties of the elements and their compounds will markedly influence the selection of the analytical technique, a brief commentary on selected properties for beryllium or cadmium emissions anticipated from known sources is included in a preface for each element. Potential analytical approaches, based on the chemical or physical properties are then presented.

Wherever specific analytical approaches have been used to monitor an element, a detailed outline of the principle, applicability, and operational parameters is tabulated. These detailed outlines generally highlight the merits and limitations of potential methods.

In several cases, candidate analytical methods have not been applied to the element of interest. As a consequence, specific information regarding operational parameters and response factors are not available. In the briefing document, the technique is described by indicating the principles involved, potential applicability, and anticipated problems.

2. SOURCES AND TYPE OF BERYLLIUM EMISSION

Natural, production, and product sources of emission have been reviewed by Durocher (ref. 1). The principal chemical forms in these emissions are elemental beryllium, beryllium oxide and mixed oxides with other elements, beryllium halides, beryllium sulfate, ammonium beryllium fluoride, beryllium-copper alloys and beryllium hydroxide.

Beryllium and its compounds (ref. 1) are relatively involatile and refractory. The oxide exhibits different physical and chemical properties, depending on the temperature at which it is calcined. High-fired (>1600°C) beryllium oxide (m.p. 2530°C) resists chemical attack and is extremely refractory. The halides (bromide - sublimes at 473°C, chloride - b.p. 488°C, and iodide - b.p. 488°C) are more volatile. Beryllium nitrate (trihydrate) has avery low boiling point of 142°C. Beryllium metal has a boiling point of 2970°C.

Based on the information presented by Durocher (ref. 1), the assumption can be made that the candidate monitoring system must be able to measure quantitatively, beryllium in a variety of chemically-bound forms which have a wide range of volatility (b.p. <500°C to >3000°C) and chemical reactivity (ranging from highly reactive to very inert).

However, more descriptive of potential air concentrations than these data are the theoretical air concentrations (Table I) of beryllium based on vapor pressures of materials tabulated by Durocher (ref. 1) from the original compilation by Tepper, et al. (ref. 2). Tepper (ref. 2) also points out that under conditions in which air is circulated over a hot vaporizing surface, larger concentrations of Be can be obtained in the air stream than those indicated by vapor pressure data alone if condensation to fume (sub-micron particulate) occurs.

Table I

THEORETICAL AIR CONCENTRATIONS OF BERYLLIUM BASED ON VAPOR PRESSURES OF MATERIALS

Compound	Temperature (°C)	Beryllium Concentration ($\mu g/m^3$)
Beryllium	885 1,060	2 200
Beryllium oxide	1,710 1,990	2 200
Beryllium oxide water vapor	1,400	0.68×10^6
Beryllium fluoride	420 525	2 200
Beryllium chloride, iodide, bromide	108 158	2 200
Beryllium borohydride	20	4.35×10^6

Although most emissions will contain beryllium as the relatively nonvolatile oxide, hydroxide or metal particulate, certain emission sources, particularly metallurgical reduction facilities, could yield the more volatile beryllium compounds in the vapor phase. The sampling and analytical systems used for monitoring these emissions must be applicable to the analyses of beryllium compounds in the form of dust, mists, and fumes.

Data for coal-fired power plants (ref. 3,4) and incinerators (ref. 5) show compositional analyses for particulate and flue gases for beryllium in power plant and incinerator emissions. Based on these data, concentrations could range from 10^{-4}g/m^3 to 10^{-6}g/m^3.

3. SOURCES AND TYPE OF CADMIUM EMISSION

The principal source of cadmium is in the refining of other metals, primarily zinc (ref. 6). Little information is available on the specific emissions of cadmium in these processes. Based on ratio analysis, cadmium sulfate, cadmium oxide, cadmium oxide-iron oxide, and cadmium sulfide were reported in zinc refinery dusts.

Almost all of the oxide, sulfate, and chloride of cadmium and most of the cadmium metal produced in the United States is consumed by the electroplating industry. Cadmium is alloyed with nickel, silver-copper, silver, zinc-tin, and lead-tin, and is used in paints (cadmium red).

Cadmium oxide sublimes at 1770°K at atmospheric pressure and evaporation occurs at 900° to 1000°C. Cadmium sulfide has a vapor pressure of 10^{-4} mm Hg @ 540°C and 1 mm Hg @ 875°C. The vapor pressure of cadmium chloride is reported as 3 mm Hg @ 618°C and 316 mm @ 930°C.

The cadmium emissions may occur principally as particulate, but under certain circumstances the cadmium may be in the gas phase.

From refuse incinerator data (ref. 5), the rate of cadmium emission is approximately 3.6 grams/hour in total dust loadings of approximately 2.8 kilograms/hour.

4. CANDIDATE ANALYTICAL TECHNIQUES

A variety of analytical techniques, including colorimetry, fluorimetry, emission spectroscopy, atomic absorption spectrophotometry, gas chromatography, and electrometric measurements have been used routinely in monitoring beryllium effluents and atmospheric pollution. Somewhat similar approaches, i.e., colorimetry, emission spectroscopy, and atomic absorption spectrophotometry, plus polarography have been applied for measuring cadmium in dusts and fumes. These procedures employ standard analytical instrumentation and require collection in an impinger, electrostatic precipitator, or on a filter followed by low-temperature ashing or acid digestion prior to the actual analytical measurement. The techniques have proven useful for first generation monitoring but require moderate to lengthy time periods for sample pretreatment, are prone to contamination from reagents and the digestion processes, and are not usable for on-site, continuous monitoring of source emissions.

The prime candidates for a continuous monitor of metal emissions from stationary sources are based on radiant energy emission or absorption, and measurement of nuclear properties and radioactivity. The techniques suitable for sensors for automated analysis are:

Emission spectroscopy
Flame photometry
Atomic absorption or fluorescence spectroscopy
X-ray emission (fluorescence)
Activation analysis
Mass spectrography

Sensitivity, speed, and selectivity make the spectroscopic techniques well suited for use in continuous monitorins systems for trace metal analyses. Several continuous monitoring systems based on the spectrographic measurement of optical emission characteristics of beryllium have been developed for measuring the beryllium levels in production or manufacturing operations.

In addition to the spectrographic methods, a photoneutron technique involving the Be^9 (α, n, γ) C^{12} reaction has been successfully applied for intermittent monitoring of beryllium contamination in air. The photoneutron technique permitted the detection of 25 μg of Be/m^3 in 30 seconds.

These methods are described briefly in the follosing subsections.

4.1 Emission Spectrographic Methods

The major concern in applying emission spectrographic techniques for continuous monitoring of beryllium involves the efficiency of the excitation source to develop quantitative and representative optical emission from beryllium particulate. Spark and arc excitation have been used with relatively good success and methods using these excitations are summarized in this section. There is some evidence for incomplete vaporization and excitation of large particulate matter and for electrode contamination. It is apparent that a higher energy source, preferably electrodeless, is desirable.

The most popular means of producing excitation for emission spectroscopy are electrical sources (arcs and sparks). High excitation temperatures provide good sensitivity for most elements. The most serious limitations, particularly with the use of arc source, are electrical instability, fractional distillation, and wandering of the arc resulting in fluctuations in temperature at the excitation zone. With spark excitation, integration of several hundred sparks during an analysis produces more reproducible results, but less sensitivity than the arc.

By using time resolved spark spectra and signal integration, the lower detection levels can be reduced by minimizing background. Measurements can be started after the initial gas spectra have faded and unwanted lines can be eliminated if they have a higher excitation potential. Hagenah (ref. 7) used a two-channel (2 wavelength) recording system and integration during the period between 29 and 44 μsec after start of each spark to improve the determination of cadmium in zinc by a factor of 4.

Improvements in stability of the d.c. arc can be accomplished through the use of cathode excitation (ref. 8) and by using a cathode cored with a material ($BaCO_3$ or Li_2CO_3) of an element with an ionization potential lower than carbon (ref. 9). Cathode excitation offers advantages in sensitivity for some non-refractory elements and gives greater precision for a number of more volatile elements in a carbon matrix. With the cored electrode, arc wander and current and voltage fluctuations are minimized, but no reduction of arc temperature occurs. The added element forms a stationary positive-ion cloud at the cathode and acts as a ballast to electron flow. In general, materials with boiling points between 1000° and 3500°C show improvement in burning characteristics.

Improved vaporization and excitation can be attained by using a dual source system. A d.c. arc is used to heat and vaporize the sample while an a.c. arc or a spark provides the energy to more efficiently excite the optical emission spectra (ref. 10).

Fluorination reactions during arc discharge excitation have been used to improve the vaporization of beryllium. By introducing fluoro-carbon polymers (Fluoroplast) (ref. 11) or filter paper impregnated with Li citrate plus HF (ref. 12) into the arc, the efficiency of vaporizing beryllium was markedly increased.

By incorporating gas-sheathed (argon or helium) arc or spark discharges, additional stabilization of the spectral excitation and improvements in sensitivity can be attained.

In the d.c. arc plasma, the discharge may be considered as two overlapping sources - a high-current arc at the cathode with a temperature near 5000°K and a compressible plasma beam with a temperature of 11,000-14,300°K. Comparative studies of conventional d.c.-arc and plasma-arc excitation show the plasma arc to be twice as precise as the d.c. arc, but the d.c. arc is considerably more sensitive than the plasma arc (ref. 13). Matrix effects were found to be less than other excitation methods; the effects of hydrochloric, nitric, and sulphuric acids were found to depend on the nature of the acid but not on the concentration. The dependency on the type of acid is less than other techniques (ref. 14).

By applying a high-frequency electric field for induction heating of heat conducting gases, excitation of optical emission spectra is obtained. Detection limits are increased for many elements. Depressive interference is reduced. The excitation atmosphere can be neutral, reducing, or oxidizing, depending on the gases used in the torch. Background and banding problems are also reduced (ref. 15).

Mavrodineanu and Hughes (ref. 15) show spectral data obtained in radiofrequency discharges for approximately 70 elements including Be and Cd. Additional spectra for carrier gases - air, N_2, O_2, CO_2, He, and H_2 are also reported. Excitation of the spectral emission was accomplished at atmospheric pressure with radiofrequency discharges obtained with (a) 30 MHz and 250W, and (b) 2450 MHz and 2 kW. The flame-like discharges originate at a conical tip at the end of a conductor forming a part of the main inductor of the tank circuit with the 30 MHz system and at the tip of a graphite electrode with the 2450 MHz system. Excellent spectral data are displayed but limited quantitative data are presented. Helium and hydrogen carrier gases are preferred because of low background and non-oxidizing media.

In a study of two types of plasma sources - d.c. arc type and the high-frequency induction type (36 MHz) - Greenfield et al. (ref. 16) concluded: The plasma source is far simpler to operate than conventional arc and spark methods and gives the high stability associated with the a.c. spark combined with the sensitivity of the d.c. arc. Particular advantages of the high frequency plasma torch are the lack of electrodes, which gives freedom from contamination and produces extremely low background. Most important is the ability to inject powdered samples directly into the plasma, over a period of time, which overcomes the problem of sample inhomogeniety by permitting integration of spectral emission and allows longer exposures than with usual powder techniques, with consequent increase in sensitivity. Also, the plasma source provides sufficient energy to overcome depressed interference effects.caused by the formation of stable compounds.

An extremely sensitive emission spectrography technique with detection limits as low as 10^{-12} gram of metal has been developed based on low wattage microwave induced plasmas (ref. 17). These sensitivities are attainable based on introduction of solid sample into an argon plasma at reduced pressure after removal of solvent or diluent vapors. The sensitivity is due in part to relatively high electronic temperatures and low spectral background, in addition to the lack of compound formation in the inert atmosphere.

The major limitation of low wattage microwave excitation is the problem of quenching the plasma when molecular vapors or gases having high ionizational potentials are introduced into the plasma. Separation of the metal elements from the sample matrix is required prior to introduction into the plasma. Total amounts of material in excess of 10^{-6} to 10^{-8} gram per second are sufficient to extinguish an atmospheric pressure argon plasma (argon flow rate 100 ml per minute) (ref. 17).

Using a laser source, samples can be analyzed that are refractory, nonconductors, or molten materials. However, this source is primarily a microsampling system, exciting a spot of 5μ to 100μ in diameter. The beam of light is focused on a spot and concentrated through a microscope objective onto the sample. Excitation of the plume produced by the laser vaporization of the sample is accomplished by an auxiliary electrode system located between the sample and the microscope objective.

In two articles, Rasberry et al. (ref. 18,19) covers the characteristic of the source and an investigation of quantitative aspects of laser-probe excitation in spectrochemical analysis. Random errors come largely from variations in laser energy and from photometric errors. Correlations were established between energy of the laser beam, size of the pit formed during excitation, and spectral intensities. The major problem in applying the laser-probe to quantitative analysis is the lack of suitable standards.

Runge et al. (ref. 20) described the application of a giant pulse laser to quantitative analysis of major constituents of metals and nonmetals by pure laser excitation. Fairly reproducible quantitative relationships were obtained by superimposing four laser-excited exposures. For stainless steel samples, the coefficients of variation for Ni and Cr were 5.26% and 3.82%, respectively, and were indicated as being on a par with a.c. and d.c. arc methods.

Potentially, the laser excitation approach is very attractive, but at the current state-of-the-art, this approach is not practical for immediate application for a continuous, routine, monitoring system.

Reliable comparisons of detection limits for various analytical methods are difficult, if not impossible, to make. The experimental data must be accumulated objectively by the same investigator on the same type of samples without introducing bias by employing preconcentration steps, integration or non-integration of signals, desolvation, and other specialized treatments on selected techniques. There are no data which compare response characteristics of the emission spectra generated from a variety of excitation sources for samples of air particulate taken directly and continuously.

Dickinson and Fassel (ref. 21) show a tabulation of detection limits (Table II) produced by a number of excitation sources for trace metals in aqueous solutions. The data summarize the values obtained from a variety of literature sources and indicate the sensitivities in concentration units of μg/ml. Relative detection limits based on absolute values (e.g., μg of element) may be quite different depending on the quantity of solution required in the procedure and the use of desolvation steps. (Note - Evaporation of solvent and the use of small volumes - 5 μl - in the microwave plasma or flameless atomic absorption systems would permit detection of 10^{-14} g of element). The table is presented to show a comparison of mass/volume sensitivities for the excitation sources which potentially could be used to monitor air particulate emissions directly.

Problems of lesser concern involve the potential interferences and the selection of the analytical wavelengths. Sufficient resolution is needed to separate the beryllium lines at 3130.416 Å and 3131.074 Å from the mercury line at 3131.833 Å, titanium line at 3130.800 Å, the weak iron line at 3130.567 Å, and one line of the OH band, resulting from excitation of water vapor, which could interfere with the lower wavelength beryllium line. The beryllium line at 2348.6 Å can also be used, but consideration must be given to self-reversal phenomena.

Technology on a variety of excitation techniques, including the electrodeless system, is included in the briefing document to permit an understanding of the problems related to their use and the possibility of applying the technique to a continuous monitor.

Table II

MEASURED DETECTION LIMITS, μg/ml

Element	Wavelength A**	Radio-frequency Plasma* Emission	Flame Emission	Flame Atomic Absorption	Stabilized Arc or Plasma Jet	Microwave Plasma
Al	3961.5	0.002	0.01	0.02	0.1	0.03
As	2288.1	0.1	6	0.2	-	4
B	2497.7	0.03	0.3(BO)	3	0.05	0.03
Ba	4554.0	0.0001	0.001	0.05	0.3	1
Cd	2288.0	0.03	2	0.001	0.4	0.5
Ce	4186.6	0.007	10	95	-	20
Co	3453.5	0.003	0.05	0.005	3	-
Cr	3578.7	0.001	0.005	0.002	0.05	-
Fe	3719.9	0.005	0.05	0.002	0.14	0.5
Hf	3399.8	0.01	75	15	-	-
La	4086.7	0.003	0.1(LaO)	2	-	-
Ni	3524.5	0.006	0.03	0.005	1	0.3
P	2535.6	0.2	3(PO)	-	1.1	100
Pb	4057.8	0.008	0.2	0.004	4	1
Sb	2598.1	0.2	1.5	0.2	-	0.6
Sr	4077.7	0.00002	0.0002	0.01	0.07	-
Th	4019.1	0.003	150	-	-	4
V	4379.2	0.006	0.01	0.02	0.2	0.1
Zn	2138.6	0.009	50	0.0005	0.3	0.1
Nb	4058.9	0.01	0.6	5	-	-
Ta	3012.5	0.07	18	6	-	-
Ti	3349.4	0.003	0.2	0.04	-	-

*Concentration required to produce a line signal two times greater than background fluctuation.

**Wavelengths used were not always those used for results shown in columns 4-7.

4.1.1 Beryllium - Emission Spectrographic Analysis With Arc Discharge

4.1.1.1 Principle and Applicability

4.1.1.1.1 Principle - Air is drawn through a triggered intermittent arc (50 c/s) and the intensity of the beryllium doublet at 3130 Å is monitored together with the adjacent background and the ratio of these intensities is recorded on a ratio recorder.

4.1.1.1.2 Applicability - Mobile, fully automatic prototype was tested for analyzing atmospheres in plants handling beryllium. Accuracy and sensitivity were not materially affected by chemical form of the beryllium and are unaffected by sizes of particles normally encountered in atmospheric dust. Should be applicable to monitoring all forms of Be emissions.

4.1.1.2 Range and Sensitivity

Range: 1 to 100 μg/m³

Sensitivity: Limit of Detection - 1 μg/m³

4.1.1.3 Interferences

4.1.1.3.1 Chemical - Unaffected by common elements normally found at high levels in atmospheric dust, namely calcium, aluminum, silicon, iron and sodium. Vanadium, titanium and magnesium gave positive readings when present in comparatively high concentrations. Magnesium has a large effect, giving a reading equivalent to 1 μg Be/m³ when present at a concentration of 1 mg/m³. There is a direct spectral interference by mercury line at 3131.5 Å but is not sensitive enough for mercury vapor at room temperature to cause an interference. Chemical form of beryllium has no significant effect. Beryllium metal, high-fired beryllium, beryllium hydroxide, and beryllium ammonium fluoride were studied.

Care must be taken to use a monochromator with sufficient dispersion (band pass of 0.1 Å) to resolve one of the beryllium doublets at 3131.072 Å and 3130.416 Å from a titanium line at 3130.800 Å.

4.1.1.3.2 Physical - Independent of particle size at least up to 85μ which was limit of author's interest.

4.1.1.3.3 Memory Effect - Negligible effect observed up to 25 μg/m³ and 10% of previous determination at very high concentrations (100 μg/m³). Concentrations of 100 to 200 μg/m³ required three or four determinations to return to unbiased readings.

4.1.1.4 Accuracy, Precision and Stability

Insufficient data are reported to establish statistically reliable accuracy and precision, but comparison of monitor field trial data with conventional spectrophotometric analyses performed on filter paper specimens taken at the same time as monitor readings, shows good agreement. An average of approximately 150 monitor readings shows a concentration of 2.6 μg Be/m³, whereas 10 "integrated" filter samples analyzed by a spectrophotometric method indicate an average concentration of 2.5 μg Be/m³ for the concentration range of 0.7 μg/m³ to 4.8 μg/m³. Monitor readings were taken every minute, whereas filter paper specimens were collected on 10 or 20-minute periods. The more numerous monitor readings show many one-minute periods where no Be was detected, but also showed periods where concentrations reached 53 μg/m³.

4.1.1.5 Apparatus

4.1.1.5.1 Spectrographic source to produce 50 c/s arc discharge with time constant such that the discharge between the electrodes is approximately 25% of any one cycle.

4.1.1.5.2 Electrodes - 1/4-in. diameter copper and tipped with platinum (negative electrode) and a piece of 14 s.w.g. platinum wire (positive electrode) arranged such that air flow of sample is negative to positive. (Note - Copper and tungsten electrodes oxidized too quickly, resulting in high instability.)

4.1.1.5.3 Monochromator - Czerny-Turner with 30,000 lines/inch grating; 3rd order, gave reciprocal linear dispersion of 5 Å/min.; exit slit provided a 1 Å band pass.

4.1.1.5.4 Detector - Two quartz-windowed E.M.I. Ltd., photomultipliers.

4.1.1.5.5 Ancillary Equipment - Vacuum pump (used only to pull air sample at atmospheric pressure through analyzer), flow controller, flow meter, filters, calibration system, ratio recorder, synchronous sequence timer and electronic power supply.

4.1.1.6 Time Cycle for Sampling and Measuring

At a sample flow rate of 40 liters/minute, the monitor was set to complete one determination, based on a 20-second sampling time, every minute. Automatic programming provided a 25-minute cycle involving five calibration runs (blanks and standard) and 20 sample determinations.

4.1.1.7 Calibration Procedure

Primary calibration and validation of the technique was accomplished by comparing the monitor response data with analyses on the arc chamber effluent obtained on filter paper specimens with spectrophotometric techniques. Aerosols for primary calibration and for secondary calibration during automatic operation were generated by passing filtered air through a spark discharge between beryllium-copper electrodes. The average amount of beryllium evolved during the calibration period was 0.095 µg (±0.01 µg) corresponding to a concentration of 7 µg Be/m^3. No drift in the amount of beryllium was noted in three months.

4.1.1.8 Method of Sampling

Air drawn directly into excitation chamber.

4.1.1.9 Multi-element Application

Could be applied to all metal elements.

4.1.1.10 Size

Sampling head containing arc chamber, trigger unit for arc, monochromator and detectors measured 19-in. x 10-in. x 11-in. high and was connected to main console containing power supplies, vacuum pump and recorder.

4.1.1.11 Unit Output

Response converted to µg/m^3.

4.1.1.12 Safety Hazards

Moderately high electrical voltage for arc discharge.

4.1.1.13 Maintenance

Platinum electrodes should be adjusted or replaced every eight hours.

4.1 1.14 Recommendations for Method Improvement

Use of radio-frequency induction-coupled plasma should be considered to eliminate the need for the arc-excitation electrodes and the attendant maintenance.

Major restriction for arcs is the high erosion of permanent electrodes.

For improved vaporization of refractory particulate or high particulate loadings, consideration should be given to using an auxiliary heating arc or to using a hotter arc chamber of the Shumaker type (ref. 4-Section 4.1.1.15).

4.1.1.15 References

1. Webb, R. J., M.S.W. Webb, and P. C. Wildy, "A Monitor for the Quantitative Determination of Beryllium in the Atmosphere," United Kingdom Atomic Energy Authority, AERE-R 2868 (1959).

2. Webb, M.S.W., R. J. Webb, and P. C. Wildy, "Monitor for the Quantitative Determination of Beryllium in the Atmosphere," Journal of Sci. Instr. 37, pp. 466-471 (1960).

3. Webb, M.S.W., R. J. Webb, and P. C. Wildy, "A Monitor for the Quantitative Determination of Beryllium in the Atmosphere," United Kingdom Atomic Energy Authority, AERE-R 3318.

4. Shumaker, J. B., "Arc Source for High Temperature Gas Studies," Rev. Sci. Instr. 32, 65-67 (1961).

4.1.2 Beryllium - Emission Spectrographic Analysis With Spark Discharge - Solid Copper Electrodes

4.1.2.1 Principle and Applicability

4.1.2.1.1 Principle - The contaminated air stream is introduced by passing the air through the spark gap between solid copper electrodes. The intensity of beryllium spark lines at 3130.416 Å and 3131.074 Å is recorded on a 24-hr circular chart recorder and correlated with the concentration of beryllium in the air.

4.1.2.1.2 Applicability - A prototype of a mobile monitor was tested briefly in a beryllia production facility and showed moderate potential as a continuous monitoring device for work area atmospheres. Additional experimental data is needed to establish application in sites containing mercury (spectral interference) and applications to beryllium compounds other than beryllia. Most useful application would be as tolerance meter to show presence to excess beryllium, e.g., >2 $\mu g/m^3$.

The instrument has been proved to respond semiquantitatively to beryllium in the form of the oxide (as furnace fume and as dust), of the fluoride and ammonium double fluoride and as beryl ore. It has been used to determine the hazard in filling mobile containers with powdered ore, in operating a bricquetting press for furnace charges for an ammonium beryllium fluoride dryer, and for the furnaces for the decomposition of this fluoride and for the final metal production.

4.1.2.2 Range and Sensitivity

Range at maximum sensitivity is 0.5 $\mu g\ Be/m^3$ to 20 $\mu g\ Be/m^3$. The limit of detection corresponds to 0.5 $\mu g\ Be/m^3$.

4.1.2.3 Interference

4.1.2.3.1 Chemical - Possible spectral interference from mercury which has a fairly strong line at 3131.833 Å. Author discounts mercury interference by stating "....mercury vapour in amounts sufficient to cause interferences are unlikely in circumstances where beryllium was being worked with and even if it did, would of itself present a serious toxic hazard." A potential spectral interference by a weak iron spark line at 3130.567 Å was shown not to exist. No data are presented to establish presence or lack of response variations for different beryllium compounds.

4.1.2.3.2 Physical - The limited experimental data indicate that the spark source monitor records 25% lower values of Be content for atmospheric concentrations >8 μg/m³ when compared to filter specimens measured spectrophotometrically.

4.1.2.4 Accuracy, Precision and Stability

No data reported for accuracy and precision of measurement. No information regarding instrument stability is given.

4.1.2.5 Apparatus

4.1.2.5.1 Spectrograph - Modified Littrow design with grating having 14,400 lines/inch; dispersion in 1st order - 30 mm/Å.

4.1.2.5.2 Excitation Source - Uncontrolled Hilger spark source unit with 0.005 mfd capacity and 0.03 mH inductance; a 1 KVA Variac auto-transformer was used to prevent high frequency currents generated by spark discharge from producing feed-back to detection system and amplifiers.

4.1.2.5.3 Electrodes - 3.25 mm copper wire electrodes of high grade electrolytical quality sleeved with quartz tubing to within 1/8-in. of sparking surfaces.

4.1.2.5.4 Detection System - 1P28 photomultiplier and Bristol Pyromaster Potentiometer Model 440M Circular Chart Recorder (24-hr cycle) fitted with a planimeter coupled to a cyclometer fixed behind the pen drive axle to provide mechanical integration of area under the trace.

4.1.2.5.5 Ancillary Equipment - Vacuum pump, filter, calibration system, electronic amplifiers, flow meter.

4.1.2.6 Time Cycle for Sampling and Measuring

Monitoring is continuous; no provision for automatic calibration.

4.1.2.7 Calibration Procedure

Manual calibration was accomplished by generating a beryllia aerosol (particles <25 microns diameter) by passing a flowing stream of air over a bed of beryllia which is being agitated mechanically. The intensity of the beryllium spark line was correlated with independent spectrophotometric analysis of particulate collected on filters.

4.1.2.8 Method of Sampling

Air drawn directly into excitation chamber.

4.1.2.9 Multi-element Application

Could be applied to all metal elements. Authors note particularly Si, Pb, Zr, V, Cr, Cd, Tl, Ge, Sb, Al, B, and Mn in addition to Be.

4.1.2.10 Physical Dimensions

Mobile monitor measured 3-1/2 x 2-1/4 x 4-1/2 ft, weighed 200 lbs and was mounted on a hospital cart.

4.1.2.11 Unit Output

Recorder tracing convertible by calibration standard to $\mu g/m^3$; planimeter-cyclometer measurement convertible to μg/hr.

4.1.2.12 Safety Hazard

Moderately high voltage to generate excitation discharge.

4.1.2.13 Maintenance

Due to high wear, electrodes should be adjusted or replaced every 8 hours.

4.1.2.14 Recommendation for Method Improvements

Instrument is unsatisfactory for monitoring system as presently designed. Operation as tolerance meter for levels $<8\ \mu g/m^3$ is adequate. However, monitoring of levels $>8\ \mu g/m^3$ would require additional design considerations to minimize low readings at the higher concentrations and the memory effect after high readings.

The major problem was the inefficiency of the excitation system to ignite or vaporize the beryllium containing particles. Many large beryllium particles were not vaporized, resulting in low values. Also, the short period of signal integration resulted in erratic results.

4.1.2.15 References

Churchill, W. L. and A.H.C.P. Gillieson, "A Direct Spectrographic Method for the Monitoring of Air for Minute Amounts of Beryllium and Beryllium Compounds," Spectrochimica Acta, 1952, 5, 238-250.

Gillieson, A.H.C.P., "Monitoring for Toxic Dusts and Fumes," Atomics 6, 15-18 (1955).

4.1.3 Beryllium - Emission Spectrographic Analysis With Spark Discharge - Hollow Electrodes

4.1.3.1 Principle and Applicability

4.1.3.1.1 Principle - A high intensity spark discharge is used to excite the beryllium in the air sample, which is introduced through hollow electrodes. Beryllium spark excitation at 3130 to 3131 Å is detected by a photomultiplier tube and displayed on a strip chart recorder calibrated in μg Be/m^3.

4.1.3.1.2 Applicability - Instantaneous response feature and ability to operate continuously can be useful in site monitoring as a tolerance meter. Quantitative response is affected by "hash" or instantaneous noise level resulting from intermittent spark discharge.

4.1.3.2 Range and Sensitivity

4.1.3.2.1 Range - Approximately 1 to 25 μg Be/m^3.

4.1.3.2.2 Sensitivity - Detection level estimated by authors as somewhat less than 1 μg Be/m^3.

4.1.3.3 Interferences

4.1.3.3.1 Chemical - None reported, but consideration should be given to possibility of Hg spectral interference.

4.1.3.3.2 Physical - No data on particle size effects is given, but method is dependent on particle size. Atmospheric water vapor and particulates will influence spark characteristics. To reduce these effects an auxiliary spark gap, quenched by filtered air was used. Problems of deposits on optical surfaces were encountered from the action of the spark on the copper electrodes.

4.1.3.3.3 Memory Effect - No data reported. Apparently, no performance tests were made.

4.1.3.4 Accuracy, Precision and Stability

Limited data reported. For the range 1 μg/m^3 to 25 μg/m^3, the 95% confidence limit for a single measurement over this range was approximately ±1.3 μg/m^3. (Note - No allowance was made in calculations for reduced "hash" level at lower beryllium concentrations, which accounts for an estimated detection limit which is less than the observed confidence limit.)

Operational tests revealed good long term (24 hours) stability if an auxiliary spark is used to minimize water vapor and particulate effects and deposition on optical surfaces of copper from electrodes is prevented. However, intermittent fluctuations in the spark discharge cause considerable instantaneous noise (hash).

4.1.3.5 Apparatus

4.1.3.5.1 Spectrograph - 1/2-meter, Ebert-mounted grating monochromator enclosed in constant temperature box.

4.1.3.5.2 Excitation Source - Conventional laboratory spark source modified by adding heavy-duty capacitors for reliability under continuous operation and adjusted to give 1 to 2 breakdowns per half cycle.

4.1.3.5.3 Electrodes and Spark Chamber - Spark chamber contains 3/8-inch copper tubing electrodes supported on ceramic insulators. Air sample is drawn through one electrode into sample chamber. (Note - 2nd electrode could be hollow tubing or solid rod.) Use of an open optical port was necessary to overcome spattering from aerosol generated during spark action on the copper electrodes. An auxiliary spark gap (tungsten electrodes) was used to minimize water vapor and particulate interferences.

4.1.3.5.4 Detection System - Photomultiplier coupled to electrometer and, in turn, to strip-chart recorder.

4.1.3.5.5 Ancillary Equipment - Vacuum pump, filters, calibration system, flow meter.

4.1.3.6 Time Cycle for Sampling and Measuring

Monitoring of air at sampling rate of 0.088 m^3/min. is continuous.

4.1.3.7 Calibration Procedure

Primary, manual calibration was accomplished by aspirating a standard beryllium nitrate solution through a flamephotometer burner and allowing the exhaust gases to pass through the sampling port. From the solution concentration and flow rate through the aspirator, the amount of beryllium present in the exhaust gases was calculated. A manual field calibration was accomplished by using a beryllium-copper electrode as a secondary standard.

4.1.3.8 Method of Sampling

Air drawn continuously into excitation chamber.

4.1.3.9 Multi-element Application

Applicable to all metal elements.

4.1.3.10 Physical Dimensions

None available.

4.1.3.11 Unit Output

Recorder tracing convertible to μg/m^3.

4.1.3.12 Safety Hazard

Moderately high voltage to generate excitation discharge.

4.1.3.13 Maintenance

Copper-tubing electrodes could be used continuously for a 24-hr period before electrode gap required adjustment. Electrode replacement was required after several days operation.

4.1.3.14 Recommendations for Method Improvement

Needs capability to permit periodic calibration checks during a test cycle. Also, consideration should be given to improved spark stability. Questions concerning memory and particle size effects remain to be answered.

4.1.3.15 Reference

Rowan, J. H. and W. W. Lee, "An Instantaneous Direct-Reading Beryllium Air Monitor," Analytical Chemistry in Nuclear Reactor Technology, Fifth Conference, Gatlinburg, Tenn., 16-21, 1961.

4.1.4 Beryllium - Emission Spectrographic Analysis With Spark Discharge - Filter Paper Tape

4.1.4.1 Principle and Applicability

4.1.4.1.1 Principle - Samples of airborne beryllium dust were collected automatically on filter paper tape and subsequently analyzed by direct high voltage a.c. spark excitation of the tape bearing the specimen and by conventional measurements with a direct reading spectrograph set at 3131.07 Å.

4.1.4.1.2 Applicability - The system can be used for automatic analyses of ambient atmosphere for the continuous quantitative determination of beryllium particulate matter. The method is rapid, resulting in quantitative analyses in 75 seconds. When equipped with red lights and warning horn, the system has been used as a tolerance meter when the toxic limit of 2 $\mu g/m^3$ beryllium is reached.

4.1.4.2 Range and Sensitivity

Sensitivity of the unit for beryllium is better than 0.5 $\mu g/cm^3$ for a 60-second sampling period and values of 0.1 $\mu g/cm^3$ are readily obtainable. Increased sensitivity is possible by incorporating longer sample times in the operational cycle. The system was calibrated up to 20 $\mu g/m^3$.

4.1.4.3 Interferences

4.1.4.3.1 Chemical - Potential spectral interference from OH band, resulting from excitation of water used in applying a covering tape to the sample, was reported as minimal. A background signal was reported at the level equivalent to 0.1 $\mu g/m^3$. No response differences for variation in chemical form are shown.

4.1.4.3.2 Physical - No effects from particle size differences are presented.

4.1.4.3.3 Memory Effect - Memory effect was minimized by incorporating a burn-off period of 18 seconds during the 30-second sparking cycle. This sufficed for most samples; however, for high concentrations >15 $\mu g/m^3$ a clean-up period equivalent to three cycles or 3.5 minutes was required.

4.1.4.4 Accuracy, Precision and Stability

When three or four results are averaged, a precision of 5 to 10% is readily obtainable. Long-term laboratory-obtained precision data are reported as about 20% at the 95% confidence level.

4.1.4.5 Apparatus

4.1.4.5.1 Sampling System - An automatic filter tape drive mechanism is used to sample the air, remove particulate, and advance the tape specimen into the spark gap.

4.1.4.5.2 Spectrograph - N.S.L. 0.5-meter plane grating type, 55,000 lines/inch grating blased, 2nd order; slit width of 40 microns (entrance) and 80 microns (exit).

4.1.4.5.3 Electrodes - Copper capped with 1/16-inch platinum; 5/16-inch diameter (lower) and 1/5-inch diameter (upper). (Note - Platinum capping minimized erosion and lowered background.)

4.1.4.5.4 Detector - Photomultiplier photocell 1P28-RCA with signal amplification by an electrometer input d.c. amplifier. Signal is integrated over the exposure period by a summing condenser positioned in the feed-back circuit.

4.1.4.5.5 Ancillary Equipment - Vacuum pump, flow meters, filters, recorder and electronic power supplies.

4.1.4.6 Time Cycle

By programming overlapping events, an average time cycle of 75 seconds is attained.

The sequence of operations is as follows: (1) sample collection - 60 sec., (2) tape advancement and application of protective coating - 5 sec., (3) sample excitation - 30 sec., (4) recording data - 5 sec., and (5) reset - 5 sec. Although the sample excitation is 30 seconds, exposure time consumes only the first 12 seconds, whereas the last 18 seconds are used to burn off any electrode contamination.

4.1.4.7 Calibration

Three methods were used:

(a) Beryllium oxide mixed at varying concentrations with graphite were weighed (1 mg) directly on the tape.

(b) Known amounts of beryllium oxide were dispersed in water by ultrasonic agitation, 10 µl aliquots were pipetted on filter paper discs (0.25-in. diam.) backed with impervious masking tape, and dried by infrared heat at 29°C.

(c) Acetate solutions of beryllium were substituted for the oxide after initial calibration to provide a rapid routine check.

4.1.4.8 Method of Sampling and Sample Preparation

A filter tape (glass and asbestos type) system is used to sample air at 50.7 liters/minute. (Note - The authors believed that a flow rate of this level was necessary to minimize the sampling error anticipated with a random particle size distribution.) Dust is collected in a 9-mm circular area. At the conclusion of the sampling period, the tape is advanced automatically to the spark gap for excitation. During the advance a layer of water-activated adhesive paper is applied to the filter paper as a protective coating.

The filter tape has a minimum retention of 95% of 0.3 micron dioctyl phthalate smoke particles.

4.1.4.9 Multi-element Application

Technique can be applied to all common metal atmospheric pollutants.

4.1.4.10 Physical Dimensions

Although size and weight factors are not given and the system is considered mobile, the spectrometer used is quite large and relatively heavy.

4.1.4.11 Unit Output

Data are displayed in three forms:

(a) A panel meter indicates the beryllium in air content ($\mu g/m^3$) at all times during the exposure.

(b) A red light and warning horn operates when the toxic limit of 2 $\mu g/m^3$ beryllium is reached.

(c) A strip chart recorder indicates the successively obtained beryllium concentrations in air for periods up to 8 hours.

4.1.4.12 Safety Hazards

Moderately high voltage required for spark discharge.

4.1.4.13 Recommendations for Method Improvement

To be useful as a stack monitor, the physical size must be reduced and the monochromator system replaced, if possible, with an interference filter system or smaller monochromator unit.

The effect of the chemical form of beryllium needs to be evaluated.

4.1.4.14 Reference

Rozsa, J. T., J. Stone, O. W. Uguccini, and R. E. Kupel, "Beryllium Air Monitor," Applied Spectroscopy 19, (1), 7-9 (1965).

4.1.5 Beryllium - Emission Spectrographic Analyses With Spark Discharge Directly on Filter Paper

4.1.5.1 Principle and Applicability

4.1.5.1.1 Principle - Beryllium is determined spectrographically on air sample filter papers by direct sparking of the filter paper mounted on a silver disk which revolves on a rotating platform electrode apparatus eccentric from a silver counter electrode. The intensities of beryllium lines are measured at 3130.42 Å and 3131.07 Å and compared to a molybdenum internal standard (3132.59 Å).

4.1.5.1.2 Applicability - The method was developed as a manual operation but is extremely fast and precise with a minimum of sample handling. The technique can be used with filter samples containing as little as 1×10^{-9} g of beryllium.

4.1.5.2 Range and Sensitivity

4.1.5.2.1 Range - Reported calibration range 1×10^{-9} g to 1×10^{-8}, but can be adapted to higher levels.

4.1.5.2.2 Sensitivity - Detection limit of 1×10^{-9} g.

4.1.5.3 Interferences

4.1.5.3.1 Chemical - None reported.

4.1.5.3.2 Physical - None reported, but particle size effects are mentioned as possible interferences.

4.1.5.3.3 Memory Effect - If the filter paper containing beryllium is removed from the electrode after sparking for one revolution, beryllium "memory" lines are observed until additional electrode sparking is continued for five revolutions.

4.1.5.4 Accuracy, Precision and Stability

Lack of certified standard samples precludes determination of accuracy. Repeatability of measurements gives 5% standard deviation at the 5×10^{-9} g and 1×10^{-8} g levels and 14% at 2×10^{-9} g.

4.1.5.5 Apparatus

4.1.5.5.1 Spectrograph - Jarrell-Ash Ebert, 3.4 m, 15,000 line/in. grating with slit width of 30 microns.

4.1.5.5.2 Excitation Source - Jarrell-Ash Varisource, high voltage spark, five discharges per half cycle.

4.1.5.5.3 Detection System - Photographic emulsion.

4.1.5.5.4 Electrodes - High purity Ag disks, 1-1/8 in. diameter, 1/8-in. thick; Counter-High purity Ag rod, 5/16-in. diameter, 2-in. length, flat topped.

4.1.5.5.5 Air Sampler - Filtron portable air sampler with 5 cfm blower and 1-in. diameter filter holder.

4.1.5.5.6 Filter Paper - One-inch diameter Whatman No. 40 filter papers were used for the analyses. Glass fiber filters gave poorer sensitivity, apparently due to the fact that the paper was only partially consumed by the spark. Millipore filters present difficulties in the addition of the internal standard and in the preparation of standard samples.

4.1.5.5.7 Ancillary Equipment - Rotating platform electrode assembly, densitometer.

4.1.5.6 Time Cycle - Sampling and Measuring

Sampling time is variable and is limited by the time required to collect at least 1 x 10^{-9} g Be. Sparking time is 60 seconds. Mounting of filter paper on electrode would take approximately 60-120 seconds. Developing of the photographic emulsion and measurement of line density would take approximately 15-30 minutes.

4.1.5.7 Calibration Procedure

Each filter paper was pretreated with 10 μg of molybdenum as an internal standard. The molybdenum is added by pipetting 100 μl of solution, containing 100 μg/ml Mo in dilute H_2SO_4 onto each filter paper. (Molybdenum solution spreads uniformly through the filter paper.) The paper is dried at room temperature.

Standard samples are prepared in the same fashion by adding solutions containing beryllium and molybdenum to the filter papers, to give 2, 5, or 10 mμg Be in addition to the 10 μg Mo per filter paper. High purity molybdenum metal and high purity BeO were dissolved in analytical reagent grade H_2SO_4 to prepare the solutions.

4.1.5.8 Method of Sampling and Sample Pretreatment

Samples were taken on 1-inch diameter Whatman No. 40 filter papers with a Filtron air sampler equipped with a 1-inch diameter filter holder (Gelman Instr. Co.) and pumping 5 cfm.

For the spectrographic measurement, the filter paper was mounted on the silver disk electrode with double-sided masking tape, 1-1/2 inch width, in which a 7/8-inch diameter hole has been punched. The tape was placed on the disk electrode with the hole concentric and the filter paper was pressed on the tape. A separate disk, freshly cleaned in concentrated reagent grade H_2SO_4 at room temperature was used for each analysis.

Sparking was accomplished on an offset rotating platform for 60 seconds at rotating speeds of 5 rpm. The filter paper is consumed after one revolution, but a total of five is needed to remove residual Be.

4.1.5.9 Multi-element Application

Technique could be used for most common metals found as air pollutants.

4.1.5.10 Physical Dimensions

No physical dimensions are given. However, the spectrograph used in this study is a relatively large analytical instrument.

4.1.5.11 Unit Output

Calibration data yields a data output in mμg which can be changed to beryllium concentration in air by dividing by the volume of air sampled.

4.1.5.12 Safety Hazards

High electrical voltages required to generate spark discharge.

4.1.5.13 Recommendation for Method Improvement

Although the method was devised for manual operation, suitable addition of mechanical manipulative devices could make the technique automatic for sampling and sample preparation.

4.1.5.14 Reference

Wheeler, G. V., W. A. Ryder, and K. R. Arnold, "Analysis of Air Samples for Beryllium by the Rotating Platform Spectrographic Technique," Applied Spectroscopy 16 (1), 17-19 (1962).

4.1.6 Beryllium - Emission Spectrographic Analysis With A.C. Arc

4.1.6.1 Principle and Applicability

4.1.6.1.1 Principle - An emission spectrographic method using a sustaining a.c. arc was developed based on excitation of beryllium volatilized from a chloride matrix to attain sensitivities as low as 0.001 microgram. The beryllium line at 2348.6 Å was used.

4.1.6.1.2 Applicability - Method is a manual technique developed for analysis of beryllium in air particulate, ores, and biological materials. In its present form the technique is not applicable to continuous monitoring of stationary source emissions. However, the technology developed during the method development can be used to increase response factors, to better understand and minimize volatilization problems, and to improve precision and accuracy of analyses.

4.1.6.2 Range and Sensitivity

4.1.6.2.1 Range - Reported as 0.001 microgram to 0.1 microgram.

4.1.6.2.2 Sensitivity - 0.001 micrograms.

4.1.6.3 Interferences

4.1.6.3.1 Chemical - A delayed volatilization results from the presence of salts of Na and K (salts of alkali metals above lithium). A suppressing effect on the intensity of trace element spectra produced in an a.c. or d.c. arc can result from the presence of these alkali metals due to their low ionization potentials. The authors demonstrate the repressive effect on volatilization by using a ratio of 0.1 μg Be to 4 mg of salt. The presence of chloride ion (Li salt, but not Na or K salt) increases volatilization.

4.1.6.3.2 Physical - Response depends in large part on the volatility of the beryllium compound.

4.1.6.3.3 Memory Effects - With the d.c. arc, complete vaporization of beryllium can take approximately 120 seconds. By using the sustaining a.c. arc and chloride buffer, the volatilization and excitation of 0.1 μg Be were essentially complete in 90 seconds, and approximately 98% complete in 75 seconds.

4.1.6.4 Accuracy, Precision and Stability

An evaluation of the total analytical scheme, including wet ashing, over a six-month period for samples containing 0.001 to 0.100 microgram quantities of beryllium, gave a mean coefficient of variation of 13.9%.

The accuracy was evaluated by applying the total procedure to eight beryllium ore samples analyzed previously by the Bureau of Mines using a quinalizarin method. For six samples the % deviation ranged from 0.1-9.4% and for the remaining two the % deviation varied from 13.6% to 15.8%. The ore specimens contained 0.1 to 3.1% Be and minute aliquot ranging from 1:100,000 to 1:2,500,000 were taken for spectrographic analysis.

4.1.6.5 Apparatus

4.1.6.5.1 Spectrograph - Bausch and Lomb large Littrow type spectrograph with quartz optics, condensing lens system, and a 20-micron slit.

4.1.6.5.2 Excitation Source - NSL sustaining a.c. arc Model PE 7090 operated at 18 amp.

4.1.6.5.3 Electrodes - Regular grade, spectroscopic graphite electrodes, 5/16-inch diameter.

4.1.6.5.4 Detection System - Photographic plate.

4.1.6.5.5 Ancillary Equipment - Densitometer, micropipet assembly, air particulate samplers (filter, impinger or electrostatic precipitator).

4.1.6.6 Time Cycle

A 90-second excitation period was used. Total analysis time is approximately 45 to 60 minutes.

4.1.6.7 Calibration Procedure

Beryllium standards were prepared from $BeSO_4 \cdot 4H_2O$ in 1:1 HCl diluted with water. The pH of each solution was maintained between 1 and 2 to prevent deposition of beryllium on the walls of the glassware. The intensity ratio of the Be 2348.6 Å line and the background on the higher wavelength side of the beryllium line were recorded and correlated with the amount of Be used for calibration.

4.1.6.8 Method of Sampling and Sample Pretreatment

Samples can be obtained as residues on filters, or impinger solutions. No details are given for collecting air particulate specimens. The sample pretreatment involves wet ashing, conversion to chloride form, and dissolution in water. The liquid was deposited on waterproofed electrodes to which LiCl-graphite buffer was added.

4.1.6.9 Multi-element Application

Technique can be applied to most metal elements encountered as air pollutants.

4.1.6.10 Physical Dimensions

No data are given, but a large laboratory spectrograph was used.

4.1.6.11 Unit Output

Data output is presented as micrograms of Be.

4.1.6.12 Safety Hazards

High electrical voltages are used to generate the electrical arc.

4.1.6.13 Recommendations for Method Improvement

In its present form, the method is not applicable to continuous monitoring. However, the technology regarding the sustaining a.c. arc and the improved volatilization of Be should be useful in other spectrographic techniques.

4.1.6.14 Reference

Keenan, R. G. and J. L. Holtz, "Spectrographic Determination of Beryllium in Air, Biological Materials, and Ores Using the Sustaining A.C. Arc," Am. Ind. Hyg. Assoc. J. 25, 254-263 (1964).

4.1.7 Cadmium, Chromium, Copper, Lead, and Nickel-Emission Spectrographic Analysis With Spark Discharge

4.1.7.1 Principle and Applicability

4.1.7.1.1 Principle - A spectrographic technique for the direct measurement of elements of airborne dirt collected on filter paper has been developed. The technique is not continuous, but requires separate collection and analysis systems. The filter paper is manually transferred to the spectrograph after folding the paper into a cylindrical form. By using a push-up electrode system, the cylindrical filter paper is forced through a hollow graphite electrode into the spark gap where the filter paper is consumed in an oxygen atmosphere and the metal elements are excited to optical emission.

Spectra are produced and recorded on a direct reading spectrograph interfaced with an IBM 026 card punch.

4.1.7.1.2 Applicability - The method was devised to monitor dirt level in manufacturing facilities for controlling airborne contamination and to measure twelve elements which can be related to the source of contamination in the manufacturing atmosphere. Correlation of the dirt level observed in manufacturing areas were made with work schedules, machine wear, and air conditioning efficiency.

4.1.7.2 Range and Sensitivity

4.1.7.2.1 Range

Element	Wavelength (Å)	Range (μg)
Cadmium	2288.02	0.1-100
Chromium	3021.56	0.1-100
Copper	3247.54	0.1-25
Lead	2833.07	0.1-100
Nickel	3002.49	0.1-100

4.1.7.2.2 Sensitivity - A detection limit of 0.1 μg is reported for each element.

4.1.7.3 Interferences and Sources of Contamination

4.1.7.3.1 Chemical - Analytical curves were S shaped, showing a toe effect at the lower concentration which is attributable to background and residual element in the filter paper. The shoulder at the higher concentration may be due to incomplete sample excitation and self-absorption. Curves are linear over the 0.3-10 μg range.

Care to avoid contamination when preparing the filter paper is required. Improper manipulation of the filter can result in considerable error.

4.1.7.3.2 Physical - None are mentioned directly, although there is a suggestion that incomplete sample excitation may occur. No data showing possibility of particle size effects are presented.

4.1.7.3.3 Memory Effect - None with replaceable electrodes.

4.1.7.4 Accuracy, Precision and Stability

Precision is approximately ±25% of the amount present at the 3 μg level.

4.1.7.5 Apparatus

4.1.7.5.1 Spectrograph - Baird-Atomic 3 m research direct reading, model GX-1, 1200 grooves/mm, 1st order with Baird-Atomic Spectrosource, model NB-1.

4.1.7.5.2 Electrodes - (a) sample - 1/4 in. x 1-1/2 in. high purity graphite, drilled axially 1/8 in. diameter through length of electrode; (b) counter - high purity graphite.

4.1.7.5.3 Excitation - High voltage a.c. spark with 6 breaks/half-cycle.

4.1.7.5.4 Detector - Photomultiplier of 1960-3300 Å range and 14 channel digital clock read-out.

4.1.7.5.5 Push-up Assembly - Cardiod cam and push rod.

4.1.7.5.6 Oxygen Distribution Nozzle - 30 ft^3/hr.

4.1.7.5.7 Sample Collector - (a) 25-mm diameter filter paper (Schleicher and Schnell type 589-1H) in nylon filter holder with stainless steel support screen, retaining particles >0.5 micron; (b) membrane-type filter - Millipore Filter Corp. or Gelman Instrument Co. (Note - These brittle and flammable membrane filters had to be prepared by rolling the membrane together with a filter paper or dissolving the membrane on the paper.)

4.1.7.5.8 Ancillary Equipment - Vacuum pump, tubing, motor drive for push-up electrode system, computer interfacing.

4.1.7.6 Time Cycle for Sampling and Measuring

4.1.7.6.1 Sampling - Time adjusted to fit calibration curves.

4.1.7.6.2 Measuring - Excitation period 30 seconds for a total analysis time of 5 minutes.

4.1.7.7 Calibration Procedure

Standard filter papers were prepared by solution addition of the elements to blank filter papers. All elements except silicon were combined in a single solution. Standards for silicon were prepared using reagent-grade sodium metasilicate in distilled water. Standards were exposed in quadruplicate and analytical curves were drawn relating Baird digital clock readings to log of concentration. Equations (5th order) of these curves were determined and programmed into an IBM S/360 model 65 computer.

4.1.7.8 Method of Sampling and Sample Preparation

For routine ambient atmosphere sampling, a steam or compressed air ejector (Graham Mfg. Co., Inc.) was used to provide a vacuum of 15 in Hg and a flow rate of 0.5 ft^3/min. Flow control was accomplished with an orifice of 0.045-inch in diameter. Collection efficiency was 95% or better on all particles larger than 0.5 micron.

4.1.7.9 Multi-element Application

Applicable to all common metal pollutants.

4.1.7.10 Physical Dimensions

Not given, but spectrograph is a large research laboratory model.

4.1.7.11 Unit Output

Micrograms of element and a five digit profile number based on the percentiles of certain elements in the total dirt. Each digit of the profile number indicates to nearest 10%, the proportion of the total contributed by a particular element or group of elements, e.g., 1st digit - iron; 2nd digit - copper; 3rd digit - zinc, tin, and lead; 4th digit - calcium, magnesium, and silicon; and the 5th digit - chromium and nickel.

4.1.7.12 Safety Hazard

High voltage spark source.

4.1.7.13 Recommendations for Method Improvement

As described, the technique is obviously not suitable for continuous monitoring. Although a mechanical means of folding a filter and introducing the specimen through a cored electrode may possibly be developed, this method of handling the sample filter does not appear practical for an unattended, automatic analyzer.

4.1.7.14 Reference

Lander, D. W., R. L. Steiner, D. H. Anderson, and R. L. Dehm, "Spectrographic Determination of Elements in Airborne Dirt," Applied Spectroscopy 25(2), 270-275 (1971).

4.1.8 Emission Spectrographic Analysis for Cadmium With a Microwave Induced Argon Plasma

4.1.8.1 Principle and Applicability

4.1.8.1.1 Principle - A non-flame cell using a low power (20-70 W) microwave induced argon plasma at atmospheric pressure was used for emission spectroscopic measurements. The method was tested on a number of elements, but principally on cadmium (228.8 nm). A rapid electronic amplifier/integrator system was used to follow the weak and transient emission signals.

4.1.8.1.2 Applicability - The method was demonstrated as applicable to detect zinc, antimony, selenium, arsenic, lead, cadmium, iron, iodine, copper, boron, beryllium, and mercury down to 10^{-9} to 10^{-13} gram of metal in aqueous solution. Quantitative measurement of cadmium was performed over the range 0.01-5.00 μg Cd ml^{-1}. It was not possible to study concentrations above 5.00 μg Cd ml^{-1} with the electronic integrator. Method used minute amounts of sample (0.12 μl).

4.1.8.2 Range and Sensitivity

4.1.8.2.1 Range - Cadmium, 0.01-5.00 μg Cd ml^{-1}.

4.1.8.2.2 Sensitivity

Element	Detection Limit (g)
Cadmium	2.0×10^{-13}
Beryllium	1.2×10^{-10}
Zinc	8.0×10^{-11}
Antimony	5.0×10^{-10}
Selenium	4.0×10^{-10}
Arsenic	4.2×10^{-11}
Lead	1.2×10^{-10}
Iron	3.0×10^{-10}
Iodine	1.2×10^{-9}
Copper	1.2×10^{-10}
Boron	1.2×10^{-10}
Mercury	1.6×10^{-11}

4.1.8.3 Interferences

4.1.8.3.1 Chemical and Spectral - Vanadium, present in the form of ammonium metavanadate at 1000-fold molar amounts compared to cadmium, interfered giving a 40% reduction in signal intensity.

At concentrations of 1000-fold molar amounts, phosphate, silicate and aluminum did not interfere.

When cadmium solutions containing 0.25 μg Cd ml^{-1} and other elements in 1000-fold molar amounts were analyzed, only arsenic showed moderate spectral interference from the 228.812 nm direct line emission. No interference was observed from either cobalt (228.781 nm) or antimony (228.898 nm) when present in a 1000-fold molar amount compared to cadmium.

Most useful portion of spectrum is below 300.0 nm where the plasma background is lowest.

A light leak in the spectrophotometer resulted in distorted integrated emission signals when cadmium solutions containing sodium ($\geq$ 5000 μg/m^{-1}) were analyzed.

4.1.8.3.2 Physical - Arsenic evaporation from the platinum filament occurred in several stages: (a) at room temperature, and (b) at various filament temperatures. These data suggest that variations in emission intensity could depend on the volatility of the species.

4.1.8.4 Accuracy, Precision and Stability

Precision data were obtained by analyzing thirty solutions containing 0.25 μg Cd ml^{-1}. The relative standard deviation was 10%.

4.1.8.5 Apparatus

4.1.8.5.1 Spectrograph - Unicam SP900 spectrophotometer.

4.1.8.5.2 Excitation System - "Microton 200" microwave generator (2450 ± 25 MHz) with Evenson type 1/4 λ cavity producing stable plasma with powers ranging from 20-75 W and optimized at 40 W, plasma cell, platinum or tungsten filament for sample vaporization, and Tesla coil ignitor.

4.1.8.5.3 Detection System - EMI 9601B photomultiplier with specially designed rapid amplifier/integrator unit (see reference) and Servoscribe recorder.

4.1.8.5.4 Ancillary Equipment - Argon supply, flow controller and flowmeters.

4.1.8.6 Time Cycle for Sampling and Measuring

No data given; excitation time is <2 seconds; sample time including evaporation of solvent is estimated as <2 minutes.

4.1.8.7 Calibration Procedure

Standard solutions were prepared from analytical-grade chemicals and deionized water. Ten samples at each concentration were vaporized into the plasma and the emission intensities were averaged. A log/log curve of signal vs concentration was plotted. The normal analytical working curve was linear over the concentration range 0.01-5.00 µg Cd ml^{-1}. It was not possible to study concentrations above 5.00 µg Cd ml^{-1}, due to electronic saturation of the integrator.

Calibration curves constructed without using the integrator were not reproducible and were non-linear; the signal increased 4-fold for a 1000-fold increase in concentration.

4.1.8.8 Method of Sampling and Sample Preparation

Aqueous solutions (0.12 µl) were retained on an elliptical platinum wire loop by a surface tension film. The aqueous film was evaporated first by passing a 0.1 amp d.c. current through the filament. Then the current was increased to 1.9 amp which caused the compound remaining on the loop to vaporize and pass into the plasma region. Tungsten loops were used when a higher volatilization temperature was required.

4.1.8.9 Multi-element Application

Technique can be used for all metallic and non-metallic elements. The principal problem is the method of sample introduction and potential losses of very volatile elements or compounds.

4.1.8.10 Physical Dimensions

None given, but spectrometer is medium sized laboratory instrument.

4.1.8.11 Unit Output

Output expressed in weight units, grams or micrograms. Data can be converted to mass/unit volume.

4.1.8.12 Safety Hazard

Moderate voltages in electronic amplifier.

4.1.8.13 Recommendation for Method Improvement

Amplifier/integrator system should be modified for higher signal capacity.

Method is not directly applicable to continuous monitoring of stack emissions. Modifications of sample introduction system are required. The use of a metal frit or electrostatic collector should be considered.

4.1.8.14 Reference

Aldous, K. M., R. M. Dagnall, B. L. Sharp, and T. S. West, "A Microwave-Induced Argon Plasma System Suitable for Trace Analysis," Anal. Chim. Acta 54, 233-243 (1971).

4.1.9 Radio-Frequency Induced Plasma-Spectroscopic Studies

4.1.9.1 Principle and Applicability

4.1.9.1.1 Principle - Emission spectra of various gases - argon, helium, nitrogen, air, water, argon and air, argon and oxygen, argon and nitrogen, or argon and helium - were obtained by radio-frequency (8 MHz) excitation of optical emission spectra.

4.1.9.1.2 Applicability - Technique was not devised for trace metal analyses, but the spectral data are important to determine potential spectral interferences from the sample background.

4.1.9.2 Range and Sensitivity

No data reported.

4.1.9.3 Interferences

4.1.9.3.1 Chemical - When a short coolant tube was used, the after-flame emitted band spectra characteristic of O_2,$_{+}N_2$, OH and weak bands which were apparently due to NH and N_2^{+}. When the coolant tube was very short, the secondary region extended beyond the end of the coolant tube into the atmosphere and these band systems became more prominent and the continuum increased. The results of this torch configuration were quite similar to thse obtained when large air samples were introduced into the coolant system.

When water vapor was introduced into either the coolant or center streams, moderately strong OH bands (3064 Å) were emitted from all regions of the plasma and the overall intensity of the plasma was decreased while the amount of heat dissipated increased. Balmer-series hydrogen line were also found. These lines were very strong and quite broad from the core and secondary region and were stronger when the sample was introduced into the core than when the sample was introduced into the coolant stream. The hydrogen lines rapidly weakened in the tail-flame and disappeared before the end of the coolant tube was reached. The 2800 Å OH band was also found occasionally, but was only 10% as strong as the 3064 Å band. Low concentrations (no values reported) had little effect on the intensities of the argon lines and almost no visual effect. The introduction of water vapor into the core causes considerable increase in the intensity of the continuum and thus reduced the line-to-background ratio of the argon. The intensity of the 3064 Å OH band was found to increase from the core to the tail-flame, while the effect on the Balmer-series hydrogen was reversed. The OH bands were found to increase in intensity with increases in the radio-frequency power.

When nitrogen was introduced, the spectra obtained from all three regions of the plasma discharge (core, secondary or transition zone, and tail-flame) showed the second positive nitrogen system and at higher power levels, particularly from the core and secondary region, bands of the first negative nitrogen system appeared, originating with N_2^+. Atomic nitrogen lines are probably present, but are too weak to detect.

Introduction of oxygen, even at low levels, caused severe reduction in the line intensities. At higher concentrations (no levels given), a poorly developed oxygen band system appeared.

Introduction of helium had no effect on the spectrum as far as the number of emission lines and bands are concerned, but did cause a slight reduction in the intensities of the argon lines and an increase in the intensity of the OH bands and the continuum. No emission lines characteristic of helium were found.

Air introduction produced an effect which was a mixture of the effects produced by oxygen and nitrogen. Nitrogen and oxygen bands were prevalent as in the case of either gas and the line-to-background ratio decreased along with a smaller decrease in the line intensities. The OH bands became very prominent and the NOγ-system appeared. The effect of rf power on emission intensity for moist nitrogen is reported graphically.

4.1.9.3.2 Physical - When nitrogen, oxygen, helium and air [illegible]laced argon in the coolant stream, the plasma discharge was not extinguished. However, with some mixtures it was necessary to increase power level to 2 kVA to maintain the discharge. Pure samples of air, nitrogen, oxygen and helium in the coolant stream required approximately twice the minimum power (ca. 1.4 kVA) used for argon alone.

In the case of nitrogen and helium, all of the argon could be replaced in the center tube, but in the case of air and oxygen, pure gas samples could not be introduced into the center stream without raising the power levels.

In general, introduction of any of the gases into the center stream resulted in severe contraction of the core, a reduction in the line-to-background ratio and reduction of line and band intensities in the spectrum obtained of the core and secondary region and to a lesser extent from the tail-flame. Introduction of sample gases into the tail-flame did not affect the core or secondary region, but drastically changed the spectrum of the tail-flame.

Continuous operation was not possible at power levels above 1.75 kVA with pure argon because the plasma attacked the quartz tubing.

Considerably more sample (up to 10 times) could be handled in the coolant stream as in the center stream without extinguishing the plasma. The amount of sample introducible into the coolant stream was limited only by build-up of carbonaceous material from samples highly loaded with organic compounds or condensation in the torch head when liquid samples were used. The latter problem was minimized by operating in the discharge downward position.

Care must be taken when recording the emission spectrum from the core and secondary regions to prevent saturation of the photomultiplier.

4.1.9.4 Accuracy, Precision and Stability

Limited data are reported. Continuous monitoring of the 4201 Å argon line with the instrument set to read full-scale deflection gave a signal-to-noise ratio of 100:1 to 200:1 with maximum variation from the mean of 2% over 3 successive 20-min. runs produced over a period of 2 hours. Over short periods of time, ca. 1 or 2 days, the system may be shut down and restarted and the readings reproduced within 1-2% without adjustment of equipment.

4.1.9.5 Apparatus

4.1.9.5.1 Spectrograph - Modified Jarrell-Ash atomic absorption spectrophotometer, Model 82000 with a 0.5 m Ebert mount scanning monochromator.

4.1.9.5.2 R-F Power Unit - Lepel T-5-2-MC-J-B with 5 kVA nominal output operated at 8 MHz.

4.1.9.5.3 Excitation Source - Wendt and Fassel type plasma torch; dual-tube, laminar-flow.

4.1.9.5.4 Ancillary Equipment - Strip chart recorder, gas manifold, silica-gel drying tower, ascarite tower, argon pre-heater and oxygen stripper (3 ft x 0.5 in. copper tubing wrapped with a 800-W heater), carbon rod igniter, external spark coil, metering valves, and flowmeters.

4.1.9.6 Time Cycle for Sampling and Measuring

No data reported.

4.1.9.7 Calibration Procedure

None given.

4.1.9.8 Method of Sampling

Gaseous samples were introduced through a metering valve and rotameter into a mixing chamber where the sample was mixed with carrier gas or introduced directly into the torch without carrier gas.

Samples could be introduced into the plasma in three places: (a) center stream in which case a portion of the sample would be introduced directly into the core of the discharge, (b) coolant stream in which case most of the sample would pass by the core and only limited mixing would occur, or (c) tail-flame with or without carrier gas.

When air was examined only 2 mg/sec could be introduced into the center stream, representing a composition of 20% air and 80% argon. However, pure nitrogen (22 liter/min.) could be introduced into the coolant stream or into the tail-flame.

The flow conditions under which a plasma was sustainable were critical and are reported in detail by the authors.

4.1.9.9 Multi-element Application

Applicable to all common metal pollutants and potentially applicable to non-metallic elements.

4.1.9.10 Physical Dimensions

Not given, but spectrometer is moderately sized research model.

4.1.9.11 Unit Output

None reported.

4.1.9.12 Safety Hazard

High voltages; open flame.

4.1.9.13 Recommendations for Method Improvement

Although method was not used for metal analysis directly, the concept and technology are useful for trace element spectrographic measurements.

4.1.9.14 Reference

Truitt, D. and J. W. Robinson, "Spectroscopic Studies of Radio-Frequency Induced Plasma, Part I. Development and Characterization of Equipment," Anal. Chim. Acta 49, 401-415 (1970).

4.1.10 Emission Spectrographic Analysis With Low Wattage Microwave Induced Argon Plasmas at Atmospheric Pressure

4.1.10.1 Principle and Applicability

4.1.10.1.1 Principle - Optical emission spectra, generated by microwave (2450 MHz) induced excitation in an argon plasma, are used to measure metals in the range of 10^{-11} to 10^{-12} gram on a sample size of 10^{-5} to 10^{-6} gram. Relatively low microwave power levels of approximately 25 watts gave maximum emission intensities for volatile metal salts or organometallics.

4.1.10.1.2 Applicability - The technique was applied to volatile copper, chromium, iron and silver compounds in solution. Results indicate that the method is extremely sensitive with detection limits as low as 10^{-12} gram of metal.

Major limitations are the upper limit of the amount of material (10^{-6} to 10^{-5} gram per second), which can be introduced into an atmospheric pressure argon plasma before the plasma is extinguished, and the low thermal temperatures of the discharge. To use samples larger than 10^{-6} to 10^{-5} gram per second, a separation or concentration step is required. Measurement of solutions is accomplished by evaporating the solvent from a sample deposited in a loop of metal filament. A secondary heating source - resistance heating of the metal filament - is used to vaporize the metal compound into the discharge zone.

4.1.10.2 Range and Sensitivity

4.1.10.2.1 Range - Approximately 10^{-12} gram to 10^{-7} gram.

4.1.10.2.2 Sensitivity - Results indicate detection limits as low as 10^{-12} gram of metal.

4.1.10.3 Interferences

4.1.10.3.1 Chemical - The mechanism of certain enhancement or depressive effects is not fully understood. The presence of another metal in the sample matrix results in response enhancement until a level of 10^{-8} gram of metal being measured is reached. However, when glycerin was added, a depressive effect on intensity was noted above 10^{-9} gram of total sample.

Presence of oxygen in the inert gas (argon) can result in formation of relatively stable molecular species.

4.1.10.3.2 Physical - Principal factors which affect sensitivity are microwave power, position in discharge, sample vaporization rate, argon flow rate, sample size and composition, and temperature of argon. Most of these factors can be optimized and stabilized; many interact with each other.

One of the most important effects is the variation of spectral emission intensity as a function of the position in the discharge. (The spectral emission is a distribution function which may have an intensity maximum anywhere over a distance of 0.1 to 5.0 cm in the discharge.) The intensity maximum shifts depending on the element being studied, on the matrix, and on sample evaporation rate. The maximum for acetylacetonates containing copper, iron, cobalt or chromium may occur within the first few millimeters of the discharge. Copper is not carried through the entire discharge, but plates out on the walls of the plasma tube. With normal sample sizes, a given tube may be used for several days without interference.

The position and intensity of the maxima are also affected by the presence of a matrix. Excitation of pure metal chelates yield lower intensities and maxima, which occur earlier in the discharge, than excitation of the same amount of metal chelates in a matrix containing another metal chelate. The analytical significance of the position effect is that intensity observations should be made in the first few centimeters of the discharge.

Considerable variation in spectral intensity occurs depending on the volatility of the sample, heating rate of the filament (for vaporizing sample) and gas flow rate. Low quantities of pure materials yield different emission intensities than the same quantity of material in a sample specimen containing other metal compounds. (Note - Addition of chromium or other metal complexes to a copper complex in sufficient quantity to yield a final sample size of approximately 10^{-6} gram minimizes interference phenomena.)

A satisfactory metallic matrix to add to silver iodide or copper chloride could not be found. It is essential that the evaporation rates be nearly equal so that both the matrix metal and sample enter the discharge simultaneously.

Since the sample is introduced into the argon stream by evaporation from a hot filament which causes some heating of the argon during the evaporation cycle, a lowering of the line emission and an increase in background can occur. This effect can be minimized by using filaments with a diameter <0.4 mm.

Plasma discharge tube was limited to 1 mm i.d. When a larger tube is used, the position of the discharge within the tube is not stable and tends to wander.

4.1.10.3.3 Memory Effects - Some plating out of metals can occur on the walls of the excitation tube.

4.1.10.4 Accuracy, Precision and Stability

Precision is such that analytically useful determinations can be made when the sample signal is 4% of the total signal (background + sample signal). The percent standard deviation at the detection limit for each metal is approximately 40%. At 10^{-10} gram, the percent standard deviation is 7%.

4.1.10.5 Apparatus

4.1.10.5.1 Spectrograph - JACO No. 82000 scanning Ebert 0.5 meter; 1180 line/mm, 3000 Å blaze, 10 micron or 25 micron fixed slits.

4.1.10.5.2 Excitation System - 100 watt microwave generator (2450 mHz), microwave coupling cavity, mount and plasma cell.

4.1.10.5.3 Detection System - Photomultiplier (1P21 and 1P28), phototube power supply, amplifier, strip chart recorder.

4.1.10.5.4 Ancillary Equipment - Argon supply, flow controller, flow meter, optical bench, lens and mounts, vaporization chamber with platinum filament.

4.1.10.5.5 Gas Purification System - Spectral interference from nitrogen was reduced by passing argon over granulated magnesium heated in a tube furnace to 550°C.

4.1.10.6 Time Cycle for Sampling and Measuring

None given; excitation time is <2 seconds. Total time for sample introduction, evaporation, and excitation estimated as <2 minutes.

4.1.10.7 Calibration Procedure

No specific technique was reported. Calibration assumed based on use of solutions of known concentrations of metal complexes (acetylacetonates) or salts in organic solvents or water.

4.1.10.8 Method of Sampling and Sample Preparation

Sample (10^{-12} to 10^{-5} gram of solid in 10 μl of organic or water solvent) is deposited on a platinum filament. After evaporation of solvent, the platinum filament is heated by passing an electrical current through the filament to vaporize the residual solid into the microwave discharge zone.

4.1.10.9 Multi-element Application

Technique is applicable to all metallic and non-metallic elements but limited somewhat by the method of introducing the sample. Modifications would be necessary depending on the sample volatility. Technique was applied principally to water or organic-based solutions.

4.1.10.10 Physical Dimensions

None given, but spectrometer system is medium sized laboratory spectrograph.

4.1.10.11 Unit Output

Output expressed in weight units, i.e., grams or micrograms. (Note - Since a specific volume of solution was analyzed, simple calculations yield mass/unit volume.)

4.1.10.12 Safety Hazard

Moderate voltages in electronic amplifiers.

4.1.10.13 Recommendations for Method Improvement

As described, the method is not applicable for a continuous monitoring system. The method of sample introduction requires that source effluent would have to be collected in an impinger system as a solution or dispersion in a liquor and subsequently introduced into the microwave discharge. Alternate possibilities include collection of particulate on a metal filter (frit) which could subsequently be heated to vaporize the sample. Care would have to be taken to prevent overloading of the discharge zone with sample, resulting in plasma quenching or inefficient excitation.

An evaluation of operation at reduced pressure (1-10 torr) should be made to determine whether improvement in response or reduction in interferences are observed. Argon was selected as a plasma gas in this study because of its monatomic character and moderate ionization potential. Low wattage microwave excitation of molecular vapors or gases with high ionization potentials to form plasmas is difficult unless the gas pressure is reduced.

4.1.10.14 Reference

Runnels, J. H. and J. H. Gibson, "Characteristics of Low Wattage Microwave Induced Argon Plasmas in Metals Excitation," Anal. Chem. 39, 1398-1405 (1967).

4.1.11. Beryllium-RF Plasma Torch - Emission Spectroscopy

4.1.11.1 Principle and Applicability

4.1.11.1.1 Principle - An inductively coupled high-frequency (36 MHz) argon plasma torch was used to excite emission spectra from which quantiative composition analyses of trace metal elements were made. Measurements were performed in the low ultraviolet region, 234.9 nm (beryllium) and 249.7 nm (boron).

4.1.11.1.2 Applicability - The system is capable of exciting the major spectral lines of trace, refractory-oxide-forming elements (Be and B) present in a powdered matrix (metal oxides). Although the technique was not applied to the direct analysis of air particulate, the solid samples were injected into the plasma from a fluidized bed and with suitable modification the system may be applicable to air particulate monitoring.

4.1.11.2 Range and Sensitivity

4.1.11.2.1 Range

Beryllium - 0.1-500 ppm in solid MgO. (Note - Deviation from linearity begins around 150 ppm.)

Boron - 2.5-1000 ppm in solid MgO. (Note - Deviation from linearity begins around 600 ppm.)

4.1.11.2.2 Sensitivity - Limits of detection (signal = 2X standard deviation of background) for beryllium and boron were 0.1 ppm and 2.5 ppm, respectively, in solid MgO.

4.1.11.3 Interferences and Sources of Contamination

4.1.11.3.1 Chemical - The effects of 10,000 ppm of aluminum, calcium, lithium, tantalum and zinc were investigated on 10 ppm of beryllium and boron in magnesium oxide, but in no instance was the variation in emission intensity significantly greater than that shown by the standard deviation for beryllium or boron alone.

Although no comments were made by the authors on the deviations from linearity of their calibration curves, the data suggest a concentration effect occurs which could be attributable to spectral self-absorption for the beryllium 234.9 nm line or incomplete vaporization and excitation of the beryllium and boron containing particles at the higher loadings.

4.1.11.3.2 Physical - None mentioned, but see 4.1.11.3.1.

4.1.11.3.3 Memory Effect - None reported, apparently not studied.

4.1.11.4 Accuracy, Precision and Stability

Relative standard deviations for 20 samples containing 10 ppm impurities added to magnesium oxide were 6.5% for beryllium and 10% for boron.

No other data are reported.

4.1.11.5 Apparatus

4.1.11.5.1 Spectrophotometer - Unicam SP900A flame spectrophotometer with entrance slit reduced to 2 mm in height. (Note - Instrument was screened from high frequency pick-up. All component packs within the spectrophotometer were grounded and all external leads were sleeved with copper braid.)

4.1.11.5.2 Plasma Generator - Frequency 36 MHz. Maximum power output 2.5 kW.

4.1.11.5.3 Plasma Torch - Brass base with two double O-ring seals and B14 socket, all concentric. Tangential gas injection for cooling and plasma flows via two quartz tubes (outer 25 mm and inner 21 mm internal diameter respectively with 1.5 mm nominal wall thickness). The outer quartz tube extends 30 mm above the inner tube and the overall torch height is 18 cm.

Gas flow rates used are: plasma flow (argon) 7.5l min^{-1}, cooling flow (nitrogen) 7.5l min^{-1} and injector flow (argon) 0.5l min^{-1}.

4.1.11.5.4 Working Coil - 2.5 turns of a 0.1875-in. square section of 20 gauge copper tubing with its ends silver-soldered to 0.25-in. BSP fittings for connection to cooling water and high-frequency power supply. The coil separation is 1.5 mm with an internal diameter of 32 mm and an outside diameter of 41 mm. Coil winding ascends anticlockwise when viewed from above (i.e., from the open end of torch). The coil is located concentrically 4 mm above the upper end of the inner quartz tube.

4.1.11.5.5 Fluidized-bed Chamber - Sintered glass disc (2 cm diameter, porosity 1) fused inside a borosilicate glass tube which is drawn out, 10 cm above and 2 cm below the disc, to 0.25-in. outside diameter tubing. The required aliquot of powder is placed above the disc and gas is injected from below.

4.1.11.5.6 Recording System - Standard galvanometer attachment to 0-1 mV strip chart recorder; galvanometer and recorder leads were converted to coaxial cable and an auxiliary 6.3 V transformer provided power for the galvanometer bulb and exterior instrument lights.

4.1.11.5.7 Ancillary Equipment - Tubing, gas flow regulators and meters, cylinders of argon and nitrogen gas.

4.1.11.6 Time Cycle for Sampling and Measuring

Total time cycle not reported. The emission intensity was recorded over a period of 30 seconds.

4.1.11.7 Calibration Procedure

Dry, powdered beryllium carbonate or boric acid was added to powdered magnesium oxide. Varying concentrations were obtained by dilution with magnesium oxide. The calibration powder was dispersed in the fluidized bed chamber and injected into the plasma torch.

4.1.11.8 Method of Sampling and Sample Preparation

Sample was introduced into the plasma torch from a fluidized bed chamber containing 3.5 g (±0.1 g) of powder. Ignition of the plasma was accomplished by inserting a carbon rod into the torch mouth. Fine adjustments of injector flow rate were made to give a prearranged recorder reading with an emission line from the matrix as an internal standard (silicon @ 251.2 nm).

4.1.11.9 Multi-element Application

Applicable to all common metal pollutants.

4.1.11.10 Physical Dimensions

Not given, but spectrophotometer is a laboratory instrument which could be made mobile.

4.1.11.11 Unit Output

Recorded as ppm of element in solid MgO.

4.1.11.12 Safety Hazard

High voltage power source; hot open flame.

4.1.11.13 Recommendations for Method Improvement

Technique could be modified with suitable flow regulation to permit direct introduction of stack gases or air for sampling. The principal problem would be to prevent quenching of the plasma. Might want to use a different beryllium line to minimize spectral self-absorption.

4.1.11.14 References

Dagnall, R. M., D. J. Smith, and T. S. West, "Emission Spectroscopy of Trace Impurities in Powdered Samples With a High-frequency Argon Plasma Torch," Anal. Chim. Acta 54, 397-406 (1971).

4.1.12 Comparison of D.C. Arc Type Plasma and High Frequency (RF) Induction Type Plasma as Spectroscopic Emission Source

4.1.12.1 Principle and Applicability

4.1.12.1.1 Principle - The principles of two types of high pressure plasma sources are described below.

In the d.c.-arc plasma jet, a closed chamber contains at one end an anode (or cathode) and at the other end a cathode (or anode) that has a small opening in it. A coolant fluid (argon) is introduced tangentially through the chamber wall and swirls around the chamber and out of the cathode hole. When the arc is struck the coolant fluid cools the outer layers of the arc so giving a "thermal pinch" effect, which causes the arc column to contract. The resultant increase in current density gives a higher arc temperature, and the pressure generated leads to the ejection of extremely hot plasma through the cathode opening, where it appears as a flame-like jet. At higher operating currents, the arc suffers a further "pinch" effect called the "magnetic pinch" due to the self-induced magnetic field. For spectroscopic purposes the substances to be analyzed is injected into the arc column and is carried out in the plasma flame.

In the high-frequency plasma torch, a stream of ionized gas (argon) contained in a circular quartz tube, surrounded by a coil carrying high-frequency alternating electric current, is heated by induction. Cold gas, being un-ionized, is not an electrical conductor and therefore the plasma torch must be externally initiated, which can be achieved by holding a carbon rod in the mouth of the quartz tube. The high-frequency field heats the carbon rod, which in turn heats and ionizes the argon. Once the main discharge has started, the carbon rod is removed and the gas stream carries the ionized gas plasma down the tube away from the coil, where it emerges at the tube mount as a "flame." To maintain the discharge, a portion of the ionized gas must be recycled. This is achieved by feeding the gas tangentially into the tube which causes a vortex, and the partial reduction in pressure at the center of this causes some of the ionized argon to move back down the tube in the opposite direction to the main gas flow.

The quartz tube described in this paper is cooled by a secondary stream of argon passing over it. When fully coupled, the high-frequency plasma can be regarded as a transformer, the work coil being the primary and the ionized gas a one-turn secondary.

The electron temperature of the d.c. arc plasma has been measured as approximately 9500°K, whereas two electron temperatures have been determined for the high-frequency thermal plasma torch. The extremely hot plasma region inside the cell has a temperature range of 12,000 to 15,000°K, and the "tail flame" region, where spectroscopic measurements are usually performed, has an electron temperature of 8000°K.

4.1.12.1.2 Applicability - Either technique can be applied to the analysis of trace metals in samples of solids, liquids and gases. Both plasma sources have high stability and sensitivity. The major advantage of the high frequency plasma is the lack of electrodes which minimizes contamination and background.

4.1.12.2 Range and Sensitivity

No absolute values of sensitivity or range are given. Sensitivity is stated as comparable to that obtained with the d.c. arc.

4.1.12.3 Interferences

4.1.12.3.1 Chemical - High excitation energy available in these sources overcame depressive effects of phosphate and aluminum ions on calcium emission at 422.7 nm. The graphite electrodes in the d.c. arc plasma produce typical arc type background; the high-frequency plasma-torch yields no intense background spectrum other than the OH band system for samples containing water.

4.1.12.3.2 Physical - None reported or studied.

4.1.12.3.3 Memory Effect - No carry-over contamination between samples if a 30-second wash with distilled water was made between exposures.

4.1.12.4 Accuracy, Precision and Stability

Only limited data are available. For the d.c. arc plasma, the standard deviation for percentage transmission of aqueous solution of 20 ppm calcium (3933 Å) is ±0.12 with a coefficient of variation of 4.5%. Note - Considering the high level of background density in this wavelength region, the source stability indicated by this figure is very good. With the high-frequency plasma torch, the standard deviation of the percentage transmission for an aqueous solution containing 100 ppm calcium (3933 Å) is ±2.3 with a coefficient of variation of 6.2%. With the calcium line at 4226 Å, the standard deviation of the percentage transmission was ±1.9 with a coefficient of variation of 4.9%.

4.1.12.5 Apparatus

4.1.12.5.1 Spectrograph - (a) Hilger large-quartz spectrograph; (b) Unicam SP900 flame spectrophotometer.

4.1.12.5.2 D.C. Arc Plasma - Modified Margoshes and Scribner plasma jet.

4.1.12.5.3 High-Frequency Plasma Torch - Modified Reed silica torch cell with 2.5 kW dielectric-heating generator operating at 36 MHz. Plasma torch was run at 1.5 kW output power.

4.1.12.5.4 Detector - Photographic plate.

4.1.12.5.5 Ancillary Equipment - Argon gas (at approximately 22 liters/minute), flow-meters and controlling device, carbon and ignition.

4.1.12.6 Time Cycle for Sampling and Measuring

D.C. arc plasma - 30-second exposures were taken on aqueous samples with a pre-spray wash time of 30 seconds. Unit was only operated continuously up to 30 minutes.

High frequency plasma torch - exposures were for 30 seconds. System is operated continuously. Test operation period was 8 hours.

4.1.12.7 Calibration Procedure

None given.

4.1.12.8 Method of Sampling and Sample Preparation

Aqueous solutions were aspirated as an aerosol into the plasma by a Unicam Atomizing unit. Powder injector for high frequency plasma torch is mentioned but not described.

4.1.12.9 Multi-element Application

Applicable to all common metal pollutants.

4.1.12.10 Physical Dimensions

None given.

4.1.12.11 Unit Output

Calibrated for ppm metal in water. Units depend on method of calibration.

4.1.12.12 Safety Hazards

High voltage and hot open flame.

4.1.12.13 Recommendations for Method Improvement

Needs additional testing with solid particulate.

4.1.12.14 Reference

Greenfield, S., I. Ll. Jones and C. T. Berry, "High-Pressure Plasmas as Spectroscopic Emission Sources," Analyst 89, 713-720 (1964).

4.2 Atomic Absorption, Thermal Emission, and Atomic Fluorescence Spectroscopy

A number of very sensitive analytical procedures based on digestion techniques, dissolution in water, and measurement of atomic absorption, thermal emission, and atomic fluorescence have been developed for the analysis of beryllium and cadmium (ref. 22-37). These techniques and others permit detection of beryllium down to 0.03 ppm with repeatability of 2% of the amount present and cadmium down to 0.001 ppm. The maximum time expenditure is 30 minutes. The methodology is based on performing analyses on liquid phases. Air particulate, collected on filters and placed into solution after a digestion process has been analyzed routinely for cadmium by atomic absorption procedures (ref. 30).

The major limitation encountered when attempting to analyze beryllium and cadmium simultaneously by conventional flame techniques (i.e., non-plasma induced) is the incompatibility of the two elements. With atomic absorption, beryllium is best measured in a very hot flame (acetylene-N_2O reducing flame) whereas the highest sensitivity for cadmium is attained with a cooler flame (acetylene-air or hydrogen-air oxidizing flame).

Although the highest sensitivity for beryllium is attained by using the nitrous oxide-acetylene flame, Fleet, et al. (ref. 33) observed signal depressant and enhancement effects by a number of other metal ions in solution. When present at the 10,000 ppm level in water, aluminum (-43.4%), silicon (-18.9%), and magnesium (-3.8%) reduced the signal intensity for a 4 ppm beryllium solution. Twenty-three other metal elements including cadmium, vanadium, iron, lead, calcium, and potassium resulted in enhancement effects up to increases of 17%. The addition of potassium to all samples produced more uniform analytical results.

Analyses of the individual elements can be improved by using sheath gases to minimize chemical reactions in the flame and background emission, but no single measurement with conventional flames will yield both beryllium or cadmium analyses with sufficient sensitivity.

Most flame techniques use sample introduction methods which provide for nebulization of a solution of the sample to form an aerosol of sufficiently small particle size which can be atomized in the flame. In most cases, direct introduction of particulate into the conventional flames results in inefficient atomization or excitation. White (ref. 38) devised an instrument, based on the atomic absorption principle, for the immediate and continuous measurement of cadmium fume under both laboratory and industrial conditions. The technique was used for cadmium fumes which by virtue of the low particle size (micron or submicron) would not settle in the inlet of the burner or would be inefficiently vaporized in the flame. This method is reported in detail in the following section.

Robinson (NAPCA Contract CPA 70-176) has a development program in progress for a flameless atomic absorption meter as a continuous air monitor. The program is based on earlier work (ref. 39) and includes radio-frequency excitation of metallic pollutants and the use of the atomic absorption phenomena to measure selected and specific elements.

4.2.1 Cadmium Analysis - Atomic Absorption Method for Cadmium Fumes

4.2.1.1 Principle and Applicability

4.2.1.1.1 Principle - A portable instrument based on the atomic absorption principle was devised which would measure the cadmium (2288Å) concentration in air. The air sample containing the cadmium fume was used to provide the oxidizing medium for a propane-air flame. Measurements were performed continuously.

4.2.1.1.2 Applicability - Continuous measurements were performed on working atmospheres in the casting shop of a manufacturer of cadmium copper (∿0.8% cadmium). The method worked well on metal fume defined as a suspension in air of micron and sub-micron particles of metals or oxides from a condensed vapour. The technique was developed for, and has been used for, metal fumes which by virtue of the low particle size will not settle in the inlet of the burner or will not be inefficiently vaporized. Apparatus was used in industrial casting shops and foundries. No data are reported for dust from machining applications.

4.2.1.2 Range and Sensitivity

The limit of detection was 0.005 mg/m^3 for cadmium, but the working range was generally 0.02 mg/m^3 to 0.2 mg/m^3.

4.2.1.3 Interferences

4.2.1.3.1 Chemical - None reported.

4.2.1.3.2 Physical - No specific details are given, but particle size greater than 1 micron may settle out or be inefficiently vaporized. Modulation of light source is required to minimize interference from light from the flame.

4.2.1.4 Accuracy, Precision and Stability

Within the accuracy limits required for the program (±10-15%), no change in calibration was noticed whenever hollow cathode lamps were replaced or other adjustments were performed.

4.2.1.5 Apparatus

4.2.1.5.1 Source of Resonance Radiation - Hollow cathode light source modulated by mechanical chopping or modulation of power supply.

4.2.1.5.2 Burner - Modified Soudgaz cartridge blow lamp; 5 cm long flame produced from propane-air mixture; burner consumed air (sample) at a rate comparable to human respiration.

4.2.1.5.3 Monochromator - Relatively simple Hilger 292 grating spectrometer.

4.2.1.5.4 Photometer - A photomultiplier sensitive to blue and ultraviolet region (RCA 1P28) and an a.c. amplifier.

4.2.1.5.5 Readout System - Panel meter.

4.2.1.5.6 Power Supplies -

Photomultiplier - Ten 90 V batteries (Ever Ready V126).

Hollow-cathode lamp - Ten 90 V batteries (Ever Ready V126) in 2 parallel stacks giving 20 ma @ 450 V. With current drain of 10 ma, a life of 20 hours is expected.

4.2.1.6 Time Cycle for Sampling and Measuring

Sampling and analysis are continuous. Checks with burner out of the optical path were made every few minutes to correct drift of monochromator or lamp intensity. Continuous operation is restricted to 2 hours by propane gas cartridge and to 20 hours by battery life.

4.2.1.7 Calibration Procedure

Apparatus was calibrated by introducing standard solutions into a conventional atomic absorption nebulizer and spray chamber to produce aerosols which were equivalent of the concentration of cadmium in air of 0.02 mg/m^3 to 0.2 mg/m^3. These aerosols were fed to the burner and the absorption was measured on a meter scale calibrated in terms of mg $cadmium/m^3$ of air.

4.2.1.8 Method of Sampling and Sample Preparation

Air was sampled directly by the aspirating effect of the blow lamp.

4.2.1.9 Multi-element Application

Instrument was applied also for measuring lead fume in air.

4.2.1.10 Physical Dimensions

Instrument was constructed as two units, measuring head (40 cm x 25 cm x 15 cm) and battery and amplifier unit (45 cm x 27 cm x 13 cm). Total instrument weight was 25 kg.

4.2.1.11 Unit Output

Milligrams per cubic meter of air.

4.2.1.12 Safety Hazard

Open flame.

4.2.1.13 Recommendation for Method Improvement

Consideration should be given to applications involving particles >1 micron. The output, depending on particle size and type of cadmium compound, needs to be better defined. Potential application to other elements should be considered. The read-out system needs improvement for unattended operation and the gas supply volume should be increased for longer uninterrupted operation. Better response could be obtained by using signal integration system.

4.2.1.14 Reference

White, R. A., "Atomic Absorption Method for the Measurement of Metal Fumes," J. Sci. Instrum. 44, 678-680 (1967).

4.3 X-ray Emission Spectroscopy

X-ray emission can be induced by application of a number of excitation sources including electron beams, higher energy x-rays, or alpha, beta, and gamma radiation from radio-isotopic sources. The simplest, less expensive, and mobile systems are those based on x-ray and radio-isotopic sources. Examples of these techniques as applied to metal analyses of air pollutants are included in this survey.

In all cases, the routine application of x-ray emission spectroscopy for monitoring air pollutants is restricted by absorption of low energy x-rays to elements with atomic numbers greater than 11. The technique has greatest sensitivity for elements in the atomic number range of 24 to 40. Detection limits vary for each element and are dependent on chemical and physical properties of the matrix. Enhancement and lowering of intensity are common problems.

The detection of beryllium by x-ray emission spectroscopy at the levels encountered as an air pollutant are virtually impossible with current state-of-the-art techniques. Measurement of soft x-rays (e.g., emitted by beryllium) has been reviewed by Holiday (ref. 40) and many of the problems and techniques encountered in these measurements are described. The application of x-ray emission techniques for the direct analysis of beryllium at the levels of stationary emission sources is not practical.

Alternate means for measuring beryllium indirectly have been developed based on the quantitative reaction with a heavier element which can be detected and measured more easily. Precipitation of beryllium as the arsenate or phosphate and x-ray fluorescence measurements of As or P yielded sensitivities of 1 µg to 40 µg (ref. 41). Although the sensitivity is high, the sample preparation techniques are too lengthy for rapid monitoring purposes.

A markedly different concept for measuring light elements by x-ray analysis has been proposed by Pichoir (ref. 42). The sample is analyzed by bombarding it with accelerated electrons (other excitation sources would also be applicable), passing the x-rays emitted from the sample through a pair of radiation filters, and measuring the intensities of the x-rays. The radiation filters are filled with gaseous fluids whose absorption characteristics are separated by only a very narrow wavelength band. During operation, the pressure of the gaseous fluids in the filters is varied so that the intensities of the x-rays outside of the narrow wavelength band coincide. This method can be used to determine the concentration of beryllium, boron, carbon, nitrogen, oxygen and fluorine, but no specific details are given for beryllium and no sensitivities are reported for any elements.

Cadmium x-rays are more energetic than those of beryllium and, therefore, can be used to measure low levels of cadmium present in airborne dusts. Several techniques based on x-ray spectrographs or radio-isotopic emission have been reported for measuring air-borne particulate collected on filters. Although electron beam and x-ray excitation of the characteristic cadmium x-ray emission have been employed for analytical purposes, the most promising excitation sources for mobile, relatively quick and inexpensive, source emission monitoring are based on radioisotopes.

X-ray emission or fluorescence dispersion techniques have been used for measuring trace metals in air-borne dust; however, no specific technique has been reported for cadmium. Cares (ref. 43) comments briefly on a comparison of the response factors of CdKα (0.54 Å), CdLα (3.96 Å), and CdLβ (3.74 Å) and matrix effects. Additional general comments on the application of dispersive x-ray emission analyses as applied to metal analyses (down to 0.5 μg) air-borne dusts in industrial hygiene studies are reported by Hirt, et al. (ref. 44).

The cadmium L-beta (3.74 Å) line is more sensitive than the K-alpha (0.54 Å), but matrix absorption, e.g., from iron, reduces the intensity of the longer wave-length line by 40% and does not affect the K-alpha intensity. In addition, a critical thickness for the L-alpha and L-beta radiations is reached at approximately 400 micrograms/cm^2. Also, higher counting losses can occur at the higher wavelengths if particles are buried in the fibers of the filter (ref. 43).

Although no specific data are reported for cadmium, the x-ray emission technique for measuring trace metals collected on filters is characterized by problems with high blanks from metals in the filter itself. Ashless and membrane filters are essentially free from contamination except for traces of iron, potassium, and calcium. Glass fiber filters have relatively high iron and zinc blanks, and contain sufficient calcium, potassium, and barium to create severe interference at or near the principal lines of those elements.

When using tungsten targets to excite x-ray fluorescence, tungsten and copper reflections from the x-ray tube produce intense interferences. Their intensities vary depending on the characteristics of the tube and the sample surface. Low concentrations of mercury, arsenic, and selenium are difficult to measure due to the intense tungsten reflections.

Relatively high sensitivities (down to 0.5 μg) for trace metals were reported (ref. 44) on specimens of air-borne dusts collected on filters. Matrix problems related to absorption of secondary x-rays, sample thickness and excessive particle size can affect the accuracy and precision of the measurement. When the total amount of sample exceeded 200 μg on a 2.4 cm (diameter) filter, considerable reduction of the x-ray fluorescence was observed. Losses were attributed to a "piling up effect" of the deposit, so that reabsorption of the secondary x-rays and lack of penetration of the primary x-rays occurred. To attain the high sensitivities, measurements had to be performed in vacuum or helium atmosphere to minimize atmospheric absorption losses. (Note - Argon K-alpha may interfere with $CdL_{\alpha\beta}$ if air path is used.)

A number of the problems related to the application of x-ray fluorescence for the quantitative measurement of trace metals in particulate can be minimized by proper selection of radioisotopic excitation sources. High resolution with semiconductor, nondispersive detector systems permit high sensitivity and specificity. However, problems of interelement, sample thickness, particle size, and spectral interferences must still be considered. Rhodes, et al. (ref. 45 or 46) reviews most of the problems related to design and application of x-ray emission analyzers using radioisotope x-ray or gamma ray sources.

Cadmium measurement over the concentration range of 0.001 to 1% in solution were reported by Hollstein, et al. (ref. 47). By using ^{241}Am (10 mCi) as the excitation source and a Si(Li) semiconductor detector, a detection limit of 0.001% of cadmium was reached in a feasibility study.

Under U. S. Atomic Energy Commission Contract No. AR-(40-1)-4205, Rhodes (ref. 48) is developing technology related to radioisotopic XRF analysis of particulate air pollutants. Preliminary results for cadmium show good instrumental precision, but data are only semiquantitative as far as absolute quantities are concerned. Cadmium excitation of K x-rays by I-125 is currently being evaluated. Rhodes, et al. (ref. 49,50) reported detection limits for radioisotope induced x-ray fluorescence determinations of 17 elements in ambient air particulate collected on cellulose filters. However, no data are reported for cadmium.

4.4 Activation Analysis

Activation analysis is widely used in measuring trace metals where high sensitivity is required. The greater proportion of these measurements are performed with thermal neutrons because of the availability of nuclear reactors and the large cross sections of nuclides for thermal-neutron capture. Sensitivities of 10^{-9} are common depending on the matrix.

Non-destructive analyses in relatively short irradiation and counting times can be performed on a number of nuclides. However, matrix effects can be severe and lengthy separation processes may be required. Severe difficulties occur when the matrix contains substantial amounts of elements with large thermal-neutron capture cross sections. A form of sample shielding results which limits the potential activation of the elements present in the sample at lower concentrations. In addition, a number of elements (beryllium, carbon, nitrogen, oxygen, iron and lead) are not highly activated with thermal neutrons.

A commercial activation analysis service reports general sensitivities, based on thermal neutron activation analysis, of 15 μg for beryllium and 0.005 μg for cadmium. However, in an air particulate sample (14 mg) collected from urban air, beryllium could not be detected and cadmium could not be measured below 9.60 μg without radiochemical separation to eliminate interferences.

Thermal neutron activation analysis, based on neutron flux from nuclear reactors is obviously not applicable to mobile operation. Although a mobile, power-free, maintenance-free activation analyses system has been developed based on a ^{253}Cf spontaneous-fission neutron source (ref. 51), the technique is not applicable to Be or Cd monitoring. Interference-free analyses are possible for 13 elements (O, Na, Al, Si, Mn, Fe, Ni, Cu, Zn, Ag, Pt, Au, and Pb), but not for Be and Cd.

Beryllium analyses with sensitivities of a few micrograms can be performed with photon activation with gamma radiation from radio-isotopic sources. Photon activation analysis was reviewed by Lutz (ref. 52), and selected techniques are evaluated in the following section.

Direct, interference-free analyses of cadmium on the average air particulate matrices are not possible with activation analysis techniques. Lengthy separation procedures are required.

4.4.1 Automatic Beryllium In Air Monitor Based on the $^{9}Be(\alpha,n,\gamma)C^{12}$ Reaction

4.4.1.1 Principle and Applicability

4.4.1.1.1 Principle - Beryllium-containing dust was removed from air with a filter tape and exposed to an alpha emitting radioisotopic source (polonium-210) to induce the nuclear reaction, $^{9}Be + \alpha \rightarrow n + \gamma + {}^{12}C$. The yield of gamma radiation is related to the beryllium content of the dust on the filter tape.

4.4.1.1.2 Applicability - The technique was developed to monitor beryllium in air on a semi-continuous basis and to yield an alarm signal when excessive concentrations were reached. The original specification for an alarm at 25, 2 and 0.01 μg of beryllium per cubic meter over periods of 30 seconds, 1 hour, and 24 hours, respectively, was not met. A concentration of 25 $\mu g/m^3$ required 4 minutes for reliable alarming and a concentration of 2 $\mu g/m^3$ required 60 minutes.

4.4.1.2 Range and Sensitivity

Both range and sensitivity depend largely on the time allotted for sampling and for counting the γ or neutron emission. Four minutes were required to reliably detect 25 $\mu g\ Be/m^3$. At the sampling rates used in the study, and the percentage of beryllium actually being measured, the detection of 25 $\mu g/m^3$, is equivalent to measuring 4.3 μg of beryllium. Statistically less reliable measurements were obtained for absolute value of beryllium at the 0.27 μg level. No upper limit was defined.

4.4.1.3 Interferences

4.4.1.3.1 Chemical - None reported; technique is generally considered free from chemical interferences.

4.4.1.3.2 Physical - The γ-detector must discriminate against the attendant gamma radiation from the alpha source. Gamma ray energy from the beryllium reaction is 4.5 mev, well above the energy of most gamma rays emitted directly from the alpha source. However, through the mechanism of gamma ray "pile up," a background gamma ray counting rate is very much in evidence (for polonium-210 sources) even though discrimination of the detector is set to reject all energies below 4.0 mev. The gamma ray "pile up" is dependent on both the energy and intensity of the attendant radiation and the amount of lead shielding employed between the reaction site and the scintillation counter.

4.4.1.4 Accuracy, Precision and Stability

The standard deviation at the 25 μg/m³ level is 40% of the beryllium count with sampling period of 2 minutes and counting time of 2 minutes. For the low level detection (2 μg/m³), the standard deviation is 86% of the beryllium count with sampling period of 2 minutes and counting time of 60 minutes.

Long term stability is questionable since the stainless steel foil window on the alpha source developed holes in a few weeks time (average of 4 weeks).

4.4.1.5 Apparatus

4.4.1.5.1 Alpha Source - Two 3-curie Polonium-210 sources.

4.4.1.5.2 Sampling System - Filter tape (Gellman Instrument Co. plastic tape), tape drive mechanism, Vacuum pump.

4.4.1.5.3 Detection System - Scintillation detector, pulse height discriminator and analyzer, alarm mechanism and power supplies.

4.4.1.6 Time Cycle for Sampling and Measuring

Time cycle is dependent on sensitivity required. Four minutes are required for reliable measurement of 25 μg/m³ of beryllium and 60 minutes are necessary for measuring 2 μg/m³. Sampling time is generally 2 minutes.

4.4.1.7 Calibration Procedure

Calibration of the beryllium monitor was achieved by analyzing tape samples chemically after measuring the gamma emission with the photo-activation system. Ten percent beryllium oxide in "Arizona Road Dust" was used in an aerosol generator to prepare standard air samples which were sampled by the filter tape system.

The calibration curve was linear from 5.0 μg to 87.0 μg.

4.4.1.8 Method of Sampling and Sample Preparation

Samples of air (79 liters/minute) were drawn through a 2-inch intake onto a 2 1/2-inch wide plastic, filter tape (Gellman Instrument Co.) for two minutes. The spot containing the specimen was advanced mechanically to the α-radiation and scintillation detector for measurement. The plastic tape samples by two mechanisms: (a) conventional filtering action through small pore sizes and (b) electrostatic collection of fine particles on its surface.

4.4.1.9 Multi-element Application

Designed only for beryllium.

4.4.1.10 Physical Dimensions

No specific details are given on the final prototype. Photographs (8) are shown.

4.4.1.11 Unit Output

Principally designed for visual and audio alarming. However, output can be related to $\mu g/m^3$.

4.4.1.12 Safety Hazard

Moderate voltages are used for electronic power supply. Deterioration of the source window can result in serious radiation hazard.

4.4.1.13 Recommendation for Method Improvement

The background of gamma rays emitted from the alpha source must be minimized. By using Pu-238 or one of the newer developed Curium alpha sources, lower attendant gamma radiation could be obtained. Better discrimination between signal and background would be possible.

Better source design based on the current state of the art should minimize the source window problem and loss of radioactivity. A safe alpha source capable of giving sensitivity in the range of at least 30 to 60 counts per minute per microgram of beryllium is needed.

Improved resolution and response of the newer semi-conductor detectors would help minimize background problems and improve sensitivity.

A larger source (at least 2 inches in diameter) would improve the efficiency of excitation. (Note - Source used in this study irradiated only 55% of the available beryllium.)

4.4.1.14 References

Braman, R. S., 1963, "Research and Development of An Automatic Beryllium-in-Air Monitor," RTD-TDR-63-1112, Air Force Systems Command, Edwards AFB, California.

Braman, R. S., 1962, "Research and Development of An Automatic Beryllium and Boron Monitor," Armour Research Foundation Final Report No. ARF 3203-3 for Air Force Flight Test Center, Edwards AFB, Calif.

4.4.2 Determination of Beryllium by the Photoneutron Method With the (γ,n) Reaction

4.4.2.1 Principle and Applicability

4.4.2.1.1 Principle - Solutions containing beryllium were analyzed by (γ,n) reaction involving photodisintegration of the beryllium nuclide. The sample is irradiated with gamma rays from ^{124}Sb and the photoneutrons produced in the reaction are counted and related to the beryllium content.

4.4.2.1.2 Applicability - The technique was applied to solutions of mixed fluoride salts, mixed beryllium and magnesium oxides with or without thorium oxide, and beryllium-copper alloys. In all cases the sample was placed into solution.

Although the method was designed for the analysis of solutions, the principle could be applied with suitable modification to monitor beryllium deposited on a filter tape mechanism.

4.4.2.2 Range and Sensitivity

4.4.2.2.1 Range - 0.1-3 mg of beryllium/ml.

4.4.2.2.2 Sensitivity - Minimum of 1.5 mg of beryllium was necessary to yield a relative standard deviation of ±1%. Although not reported, a lower detection limit could easily be reached by accepting a larger standard deviation and altering instrument parameters.

4.4.2.3 Interferences

4.4.2.3.1 Chemical - Potential interferences fall into two classes: elements having high thermal or epithermal neutron cross sections which would tend to absorb photoneutrons, and elements having high cross section for the (γ,n) reaction and might also release photoneutrons. Cadmium, which has a high thermal-neutron cross section (σ = 2500 barns), can produce a relative error of approximately 5%, depending on the Cd/Be ratio and the volume of solution. [Note - The interference is greater with larger solution volumes because water moderates the photoneutron (20 k.e.v. average energy).] A cadmium shield (0.1 in.) placed between the sample and detector screens out thermal neutrons with an attendant loss (15%) of total signal, but eliminates error from neutron absorbers. Only a few elements (Cd, Sm, Eu, Gd) have sufficiently high cross sections to interfere. Elements tested in a 20:1 ratio to Be and found not to interfere were Li, K, Cu, Zn, Ba, Al, Zr, Sn, Pb, Bi, Fe, Co, Ni, Th, V, and B.

Deuterium is the only isotope other than ^{9}Be that is capable of undergoing a (γ,n) reaction with ^{124}Sb gamma irradiation. A 24:1 weight ratio of D_2O to Be would cause a 1% relative error. (Note - A gamma source with a greater flux ^{56}Co would increase response to D_2O by two orders of magnitude.)

4.4.2.3.2 Physical - None reported.

4.4.2.4 Accuracy, Precision and Stability

Statistical data relating accuracy as measured by comparison to other techniques (colorimetry) are not given, but analyses are shown to yield comparable values.

The relative standard deviation of duplicates was ±1.1%.

Long term stability is questionable since a 400 mc ^{124}Sb (^{123}Sb irradiated) source is useful for about 2 half-lives (120 days).

4.4.2.5 Apparatus

4.4.2.5.1 Isotopic Source - 40 mg of 98% enriched ^{123}Sb irradiated for 14 days to produce 400 mc of ^{124}Sb.

4.4.2.5.2 Detector - Large BF_3 neutron counter tubes (2-inch), high voltage power supply, linear amplifier, scaler, timer, and lead shielding.

4.4.2.5.3 Ancillary Equipment - Polyethylene moderator, sample cells.

4.4.2.6 Time Cycle for Sampling and Measuring

Approximately 10 minutes required for loading and obtaining sufficient counts.

4.4.2.7 Calibration Procedure

Solutions of known concentration of beryllium are counted.

4.4.2.8 Method of Sampling and Sample Preparation

Samples are placed into solution with suitable reagents and 5-, 25-, or 50-ml aliquots are counted in the apparatus.

4.4.2.9 Multi-element Application

Specific to beryllium with ^{124}Sb irradiation, but can be applied to deuterium analysis by using ^{56}Co.

4.4.2.10 Physical Dimensions

Electronics occupy 4-ft rack and the irradiation cell is a 12-in. x 12-in. cylinder.

4.4.2.11 Unit Output

Output appears as scaler counts which are relatable to the quantity of beryllium either as mass or mass/volume units.

4.4.2.12 Safety Hazard

Electronics require moderately high voltage.

Radiation hazard depends on shielding. Operator is exposed to 100 mr/hr on hands and 50 mr/hr at head level in changing samples, but total exposure is less than 1 hr/wk. Since source activity is about 20 r/hr at 1 foot, installation must be done carefully in few seconds with 3-foot tongs.

4.4.2.13 Recommendations for Method Improvement

Technique, as presented in the publication, is not directly applicable; however, the concept can be modified to provide intermittent, <10-minute time span, measurements. Newer detection systems (semi-conductors or scintillation counters) could increase sensitivity. Consideration should be given to other isotopic sources. Sensitivities of a few micrograms are possible.

4.4.2.14 Reference

Goldstein, G., "Determination of Beryllium by the Photoneutron Method," Anal. Chem. 35, 1620-1623 (1963).

Lutz, G. J., "Photon Activation Analysis - A Review," Anal. Chem. 43, 93-103 (1971).

4.4.3 Determination of Beryllium on Air Filters With the (α,n) Reaction

4.4.3.1 Principle and Applicability

4.4.3.1.1 Principle - The (α,n,γ) reaction was used to measure the beryllium content (10 to 15 μg) on impregnated air filters. Three separate detection schemes were employed: (1) a coincident neutron and gamma system which would, in theory, eliminate background; (2) fast neutron detection with plastic scintillators; and (3) thermal neutron detection using moderated BF_3 tubes.

4.4.3.1.2 Applicability - Technique was established to measure the beryllium content on air filters. Due to escape of radioactivity from the source, the technique was not completely evaluated.

The three detection techniques were devised to minimize interferences from background, neutron and/or gamma radiation, signals. It was hoped that simultaneous measurements of both neutrons and gamma radiation produced in the (α,n,γ) reaction channeled through a coincidence gate circuit could eliminate effects of other light elements trapped on the filter. However, the sensitivity for detecting the 4.4 MeV photon, which was supposed to occur in about 60% of the reactions was insufficient.

By mounting a second fast neutron detector in place of the γ radiation detector, the output signals were channeled through an anti-coincidence gate to reduce background effects. The system was moderately effective, but high background from the Po-210 source limited the beryllium detection sensitivity.

The result of the fast neutron detection system were substantiated by a thermal neutron counting system. Although the count rate with the thermal neutron system was higher, the neutron interference from the Po-210 source limited the sensitivity to 10 μg.

4.4.3.2 Range and Sensitivity

With the Po-210 source available to the authors, it was not practical to detect <10 μg of beryllium and the desired <1 μg was not reached. No other data are reported.

4.4.3.3 Interferences

4.4.3.3.1 Chemical - Small quantities of carbon, oxygen, aluminum, sodium, etc. impurities in the filter or the Po-210 source produced high background of neutron flux.

4.4.3.3.2 Physical - No interferences based on physical properties of the sample are reported.

4.4.3.4 Accuracy, Precision and Stability

No accuracy or precision data are reported. The seal on the polonium source deterioriated over a period of 3 months, resulting in escape of radioactivity.

4.4.3.5 Apparatus

4.4.3.5.1 Isotopic Source - Alpha source (3.11 Ci Po-210).

4.4.3.5.2 Detectors - NaI crystal, photomultiplier tube and fast neutron detector; BF_3 thermal neutron counting system moderated with paraffin.

4.4.3.5.3 Ancillary Equipment - Scalers, shielding, filtering system, electronic amplifiers and power sources.

4.4.3.6 Time Cycle for Sampling and Measuring

None given; estimated <10 minutes.

4.4.3.7 Calibration Procedure

None given.

4.4.3.8 Method of Sampling and Sample Preparation

Beryllium dust was collected on filter paper and exposed to alpha radiation, but no specific details are given.

4.4.3.9 Multi-element Application

Principally designed for beryllium, although neutron flux is generated by other light elements.

4.4.3.10 Physical Dimensions

None given.

4.4.3.11 Unit Output

Signal convertible to μg Be.

4.4.3.12 Safety Hazard

High voltages for electronic power supplies. High radiation hazard due to leakage of Po-210 through cover seal.

4.4.3.13 Recommendation for Method Improvement

Better source design and the use of newer detection systems (semi-conductors) with higher resolution and sensitivity would improve the technique and permit the possible application as a beryllium monitor.

4.4.3.14 Reference

Buch, W. L. and W. G. Spear, "Measurement of Beryllium on Air Filters," AEC Contract No. AT(45-1)-1350, General Electric Co., Hanford Atomic Products Operation, Richland, Wash., 4 June 1964.

4.4.4 Beryllium - Determination by a Gamma Activation-Photoneutron Method

4.4.4.1 Principle and Applicability

4.4.4.1.1 Principle - Beryllium, in beryllium metal, beryllium oxide, and beryllium compounds, is determined by gamma activation of aqueous solutions or powder with a Sb-124 radio-isotopic source. The neutrons generated in the $^{9}Be(\gamma,n)^{8}Be \rightarrow 2\,^{4}He$ reaction are measured with helium-3 neutron detectors.

4.4.4.1.2 Applicability - Technique was developed principally as a short, precise, and economical method for measuring moderate amounts of beryllium as a major component. The technique presently is not designed for monitoring of relatively small amounts (<100 mg) of beryllium. However, the concept may possibly be modified for greater sensitivity.

4.4.4.2 Range and Sensitivity

A linear calibration curve is shown for the working range of 100-1600 mgs of beryllium with counts of $0.5\text{-}6 \times 10^{6}$ per 5 minutes.

4.4.4.3 Interferences

4.4.4.3.1 Chemical - None reported.

4.4.4.3.2 Physical - There was no significant bias in the analysis provided the powders had very similar compositions and particle sizes so that they occupied the same volume.

4.4.4.4 Accuracy, Precision and Stability

Precision of a single analysis at the 95% confidence level is ±0.2% of the value. The analyses do not differ significantly at the 98% beryllium content from results obtained by either a gravimetric or volumetric method. Source must be irradiated every six months to generate Sb-124.

4.4.4.5 Apparatus

4.4.4.5.1 Gamma Activation Source - 500-millicurie Antimony-124.

4.4.4.5.2 Analyzer - Lead pig (9" OD x 12" H) with inside cavity (7" ID x 7-1/2" H); two He-3 neutron detectors; electronic amplifiers and scaler.

4.4.4.5.3 Automatic Sample Charger coupled to the counting equipment.

4.4.4.6 Time Cycle for Sampling and Measuring

Counting is accomplished in five minutes for powdered samples.

4.4.4.7 Calibration Procedure

Calibration standards were prepared from beryllium metal (NBL F-224 from AEC, New Brunswick Laboratory, N. J.) and from beryllium oxide powder (L-33 from Kawecki Berylco Industries, Inc., Reading, Pa.).

4.4.4.8 Method of Sampling and Sample Preparation

Samples were prepared either by dissolving the beryllium sample in hydrofluoric acid, or by forming a compressed pellet. With the latter technique, the powders were compressed into stainless steel dishes (1" OD x 5/16" H) under a pressure of about five tons to form a pellet approximately 0.225-inch thick.

4.4.4.9 Multi-element Application

No others mentioned.

4.4.4.10 Physical Dimensions

No overall specifications are given. The lead pig is 9" OD x 12" H.

4.4.4.11 Unit Output

Milligrams of beryllium.

4.4.4.12 Safety Hazard

Moderate electrical voltages are used. Potential radioactivity hazard exists, but through automatic sample changing is minimized.

4.4.4.13 Recommendation for Method Improvement

Technique, as currently designed, is not applicable as an intermittent analyzer of filter paper samples of collected particulate. It is not obvious that the instrument is operating at maximum sensitivity. A trade-off of precision and improvement of the preamplifier and amplifier components may yield a more sensitive device which could be applied to analysis of filter tape specimens.

4.4.4.14 Reference

Kienberger, C. A., "Determination of Beryllium by Gamma Activation," Report Y-1733, U. S. Atomic Energy Commission, Union Carbide Corporation, Oak Ridge, Tenn.

4.4.5 Beryllium - Continuous Monitor for Air-borne Beryllium Based on the $^9Be(\alpha,n,\gamma)^{12}C$ Reaction

4.4.5.1 Principle and Applicability

4.4.5.1.1 Principle - A filter fabricated from sintered metal and incorporating an alpha emitting material dispersed throughout the filter is used to collect beryllium particulate and to measure the quantity of beryllium and the rate at which the beryllium is collected.

The beryllium particles collected by the filter react with alpha particles in the filter to yield neutrons and gamma radiation by the reactions:

$$^9Be + \alpha \rightarrow n + {}^{12}C \text{ (excited state)}$$

$$^{12}C \text{ (excited state)} \rightarrow \gamma + {}^{12}C \text{ (ground state)}$$

The yield of gamma photons and/or neutrons is measured and related to the quantity of beryllium collected by the filter.

4.4.5.1.2 Applicability - Technique can be used to provide a continuous quantitative measurement for beryllium in air or to operate an alarm mechanism to indicate an excessive concentration of beryllium in the atmosphere. The system is restricted in application as an occupational health monitor in a relatively clean atmosphere where the expected venting of particulate would be principally beryllium or its compounds. Exposure of the filter to high volume of non-beryllium particulate would cause plugging of the filter and attendant loss of efficiency and ultimately loss of sensitivity and response capability.

4.4.5.2 Range and Sensitivity

No data reported, but sensitivity estimated as less than 1 $\mu g/m^3$.

4.4.5.3 Interferences

4.4.5.3.1 Chemical - None reported.

4.4.5.3.2 Physical - Presence of excessive amounts of non-beryllium particulate could cause plugging of filter and subsequent loss of response.

4.4.5.4 Accuracy, Precision and Stability

No data reported.

4.4.5.5 Apparatus

4.4.5.5.1 Integrated Filter and Alpha Source - Filter made from sintered metal such as platinum or its oxide, or from a controlled alloy or a metalloceramic. An alpha emitting material such as polonium-210, curium-242, radium or plutonium is incorporated into the filter to provide a source of alpha particles integral with the filter and dispersed throughout. As an alternative, the alpha particle source may be plated or electrodeposited upon the filter.

4.4.5.5.2 Detection System - Sodium iodide crystal coupled with a photoelectric tube; electronic counter to read total beryllium collected; electrical differentiating to indicate rate at which air-borne beryllium is collected; alarm system.

4.4.5.6 Time Cycle for Sampling and Monitoring

Instantaneous and continuous.

4.4.5.7 Calibration Procedure

No specific details are given. Procedure would involve sampling known quantity of beryllium as suspended particulate, as an aerosol, or as a beryllium compound in solution.

4.4.5.8 Method of Sampling and Sample Preparation

Air sample is drawn directly onto the filter by means of a blower connected to the air housing outlet. No sample preparation is required. Sample could be any fluid media.

4.4.5.9 Multi-element Application

May be used to detect lithium, boron and fluorine.

4.4.5.10 Physical Dimensions

No details on size or weight are given. However, unit should be very compact and small.

4.4.5.11 Unit Output

Data should be convertible to mass, mass/unit volume, and rate of mass change.

4.4.5.12 Safety Hazard

Moderate electrical voltages. Potential radiation hazard depending on efficiencies of sealants.

4.4.5.13 Recommendation for Method Improvement

Technique should be applicable to monitoring for beryllium in a relatively clean atmosphere, but the operational lifetime in a dirty atmosphere is questionable. Consideration of replaceable filter costs is paramount.

4.4.5.14 Reference

Lamb, I. E., "Monitor for Air-borne Beryllium," U.S. 3,291,896 (1966).

4.5 Alpha Particle Scattering

Light elements can be detected by the back-scattering of a beam of alpha particles issued from a radioactive source. This principle has been applied to the detection of light elements on lunar probes and may be applied to air particulate analysis of filter collected specimens. A combination of radioisotopic induced x-ray fluorescence (heavy elements) and alpha-particle scattering (light elements) could provide a possible approach for air particulate analyses.

Some of the advantages and disadvantages of alpha particle scattering measurements are shown in the following evaluation reports.

4.5.1 Alpha-Scattering Technique of Chemical Analysis

4.5.1.1 Principle and Applicability

4.5.1.1.1 Principle - The back-scattering of a monochromatic, collimated beam of alpha particles generated in a thin radioactive source is used as a non-destructive analytical method to determine the elemental composition of solid specimens or particulate. The intensity of scattering is determined primarily by the square of the nuclear charge. For elements heavier than aluminum and for relatively low energy alpha particles, the large-angle scattering is primarily Rutherford scattering. For light elements such as carbon and oxygen, and particularly with rather high-energy alpha particles (5.80 Mev from ^{244}Cm), nuclear effects enhance the scattering above that predicted from pure Rutherford scattering.

4.5.1.1.2 Applicability - The technique has been applied for measuring light elements in rocks and on lunar missions. It is best used in a vacuum and is applicable to the study of surfaces (1 to 100 μ thick). The energy spectra of the elastically back-scattered alpha particle and spectra of protons produced by α,p reactions have been used to determine the composition of lunar rocks.

Since a single mass scatterer produces a continuous spectrum, an observed spectrum from a surface containing several elements must be decomposed into components. The high-energy end points characteristic of each mass number are unaffected by the chemical or physical state of the scatterer.

The technique can be applied for analyzing particulate on filter paper. There are some uncertainties on thickness and particle size effects. Although the technique has been applied to light elements, no specific data for beryllium are reported. There is some question concerning interacting effects of the $^{9}Be(\alpha,n,\gamma)^{12}C$ reaction.

The method has good resolution for light elements, but resolution becomes poorer as the atomic weight increases (Fe, Co and Ni cannot easily be resolved).

Using practical source intensities (ca. 100 mc), the rate of analysis is slow. A complete analysis requires about one day.

4.5.1.2 Range and Sensitivity

Sensitivity is reported as high, but no data given for beryllium.

4.5.1.3 Interferences

4.5.1.3.1 Chemical - The continuous spectra overlap and must be analyzed mathematically based on a library of spectra from pure elements. Such a library includes the response to all elements between boron and titanium (except neon, argon, and scandium) and to selected heavier elements (iron, barium and gold).

4.5.1.3.2 Physical - Response is affected by surface roughness, sample thickness, and particle size.

4.5.1.4 Accuracy, Precision and Stability

Results for most of the elements indicate absolute accuracies of about 1 atomic %.

System operated very well on lunar missions and has functioned on earth for two years.

4.5.1.5 Apparatus

4.5.1.5.1 Alpha Particle Source - 100 mc, ^{242}Cm.

4.5.1.5.2 Detector - Silicon semiconductor detectors, and suitable electronics; pulse-light analyzers.

4.5.1.6 Time Cycle for Sampling and Measuring

Measurements are performed with counting times varying from 20 to 2453 minutes. Based on lunar mission data, total processing of sample and manipulation of mathematical treatment of data can take one day.

4.5.1.7 Calibration Procedure

Calibration is based on a library of data for pure elements, mathematical adjustment of response factors, and monitoring of a standard nuclide ^{254}Es.

4.5.1.8 Method of Sampling and Measuring

Samples of airborne particulate are collected on filter paper and exposed directly to alpha radiation.

4.5.1.9 Multi-element Application

Response is observed to all elements between boron and titanium (except neon, argon, and scandium) and to selected heavier elements (iron, barium and gold). Because of poorer resolution with heavier elements, measurements reported for calcium include calcium and potassium; iron values denote elements titanium through zinc; barium analyses cover all elements heavier than zinc.

4.5.1.10 Physical Dimensions

Lunar device weighed <4 kg. The "head unit" containing the excitation source, detectors and part of the electronics was 13.3 x 17.1 x 11.7 cm and was connected by cable to an electronic package of unreported size on the Surveyor spacecraft. (Note - Due to lack of atmosphere on the moon, no vacuum system, which would be required for earth-bound operation, was included.)

4.5.1.11 Unit Output

Signal converted to atomic %, but could be converted to mass units, if desired.

4.5.1.12 Safety Hazard

Moderately high voltage for electronics. Potential radiation hazard, but system design appears to minimize the problem.

4.5.1.13 Recommendation for Method Improvement

If sensitivity requirements can be met with shorter counting periods and if the time and cost required for reducing the data can be minimized, the technique could be used for lighter elements. The application to beryllium is questionable based on potential interference from the $^{9}\mathrm{Be}(\alpha,n,\gamma)^{12}\mathrm{C}$ reaction.

4.5.1.14 References

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4.5.2 Beryllium - Measurement by Alpha-Particle Scattering

4.5.2.1 Principle and Applicability

4.5.2.1.1 Principle - An α-particle, when deflected in a close encounter with a nucleus, loses kinetic energy equal to the recoil energy of the scatterer and the loss of energy can be related to the mass of the scatterer and the angle through which the α-particle is deflected. A measurement of energy loss and deflection of particles scattered from a sample of material provides the basis of an atomic analysis of the material. By using isotopic excitation sources and surface barrier detectors, a mobile, compact apparatus was produced.

4.5.2.1.2 Applicability - By working in a modest vacuum or in hydrogen at atmospheric pressure, relatively high sensitivities can be attained for a number of elements, particularly those with low atomic numbers. Resolution of adjacent elements is possible for some, but not all elements. The apparatus described in the report produced the resolution and sensitivities (minimum sample size) tabulated below.

Element	Minimum Sample Size ($\mu g/cm^2$)*
Be	1
B	2
C	0.2
N, O	2
F	4
Na	8
Mg, Al	7
Si, P, S	6
Cl, Ar, K, Ca	5
Sc to Zn	4
Ga-Sn	3
>Sn	2

*Target of about 4 cm^2

Although the sensitivity for beryllium is extremely good, the measuring (counting) times necessary to attain this response are lengthy (1000 minutes) and are not applicable to a realistic monitoring device.

4.5.2.2 Range and Sensitivity

No specific data are given for the range of beryllium content beyond the minimum sample size of 1 $\mu g/cm^2$ (total on 4 cm^2 target of 4 μg of beryllium). Based on the limitation of sample thickness, a beryllium sample up to 150 μg/cm² (total of 600 μg on a target of 4 cm) would be the maximum amount which would yield distinct peaks for adjacent elements.

4.5.2.3 Interferences

4.5.2.3.1 Chemical - None reported.

4.5.2.3.2 Physical - To resolve the backscattered spectrum for adjacent atomic numbered elements, the sample thickness must be less than 50 μg/cm² for elements around calcium (A=40) and less than 150 μg/cm² for elements around oxygen (A=16). The spectrum from a thick target is a superposition of peaks from each infinitesimal layer in the sample and the alpha particles scattered from progressively deeper layers are attenuated more and more before leaving the sample. The superposition results in a continuous spectrum which is relatively flat with a sharp cutoff at the characteristic energy (a step display), whereas the spectrum from the thin film is characterized by individual peaks (a peak display).

4.5.2.4 Accuracy, Precision and Stability

No data reported for accuracy and precision. Erratic deterioration of the protective surface film on the source was observed. Lifetimes range from 7 days to 2 months.

4.5.2.5 Apparatus

4.5.2.5.1 Alpha Source - 0.5 mc Cm-242 source.

4.5.2.5.2 Detection System - Surface barrier detector, preamplifier, multichannel analyzer, recorder.

4.5.2.6 Time Cycle for Sampling and Measuring

Counting times for 1 μg/cm² sensitivity were 1000 minutes.

4.5.2.7 Calibration Procedure

Standard samples were prepared from known quantities of beryllium. No specific details are given.

4.5.2.8 Method of Sampling or Sample Preparation

No specific details are given. Specimens were mounted on collodion film, poly-vinylacetate-chloride and Al_2O_3.

4.5.2.9 Multi-element Applications

Technique can be applied to light elements with unit atom number resolution, e.g., Be, B, C, F, Na, and to heavier elements in combinations of two or more, i.e., N,O; Mg,Al; Si,P,S; Cl,Ar,K,Ca; Sc to Zn; Ga to Sn; >Sn.

4.5.2.10 Physical Dimensions

Specific dimensions are not given. Source and detector head is small, being less than 12 inches in diameter. Electronics would occupy approximately 4-ft standard rack.

4.5.2.11 Unit Output

Micrograms of beryllium.

4.5.2.12 Safety Hazard

Moderate electrical voltages are used in electronics. Deterioration of protective covering on alpha source presents potential radioactivity hazard.

4.5.2.13 Recommendations for Method Improvement

The lengthy counting times (1000 minutes) preclude application of the technique in present form as a short-term, immediate response monitoring device. Major improvements in the detection system and the irradiation source are necessary to maintain high sensitivity, but allow shorter analysis times.

4.5.2.14 Reference

Semmler, R. A., J. F. Tribby, and J. E. Brugger, "Application of Alpha-Particle Scattering to Chemical Analysis," COO-712-89, USAEC Contract AT(11-1)-712, October 1964.

4.6 Mass Spectrographic Analysis

High sensitivity and selectivity for metals are attainable by ion- or spark-source mass spectrometric techniques. However, analyses must be performed in a relatively high vacuum and, as a consequence, the measurements are made on a batch basis and require considerable time between samples to attain suitable conditions for efficient excitation. The technique is limited to measuring samples collected on a filtering device and is not applicable to direct and continuous source monitoring.

Additional problems related to low ionization efficiencies and spectral interferences limit the application of mass spectrographic analyses for beryllium and cadmium. Depending on the energy of the ionization source, some difficulties in attaining sufficiently high ionization efficiencies can be encountered. Generally, thermal ionization sources are inadequate and an electron impact or other ion sources are required. With thermal ionization, low efficiencies are encountered with cadmium, nickel, copper, zinc, silver, lead, tin, germanium, and silicon; whereas beryllium, phosphorus, sulphur, arsenic, selenium, tellurium, osmium, gold, polonium and palladium may not be observed (ref. 53).

With spark source excitation, considerable multi-ion fragments can be produced. Triply-ionized aluminum ($^{27}Al^{3+}$) and doubly-ionized oxygen ($^{18}O^{2+}$) can interfere with the beryllium measurements.

Brown and Vossen (ref. 54) were able to measure air pollution particles collected on special nitrocellulose filter pads for elements in the concentration range of 0.004 $\mu g/m^3$ to 40 $\mu g/m^3$ by spark source mass spectrometry. With an electrical read-out system, a survey of all elements from atomic number 92 (uranium) to atomic number 3 (lithium) can be made in a scanning time of 9 minutes. The operations involved in changing specimens and re-establishing operating conditions take approximately 10 minutes. Combustion of the filter, addition of internal standard (silver nitrate), and preparation of the sample with graphite in the form of a conducting electrode takes approximately two hours. Results for 28 elements, but not for beryllium or cadmium, were reported.

Analyses for cadmium and 61 other elements (but not beryllium) were performed by Morrison and Kashuba (ref. 55) on simulated lunar samples by spark source mass spectrometry. The technique, although lengthy, provided for the detection of 0.3 ppm cadmium. The $^{9}Be^{+}$ ion was obscured by $^{18}O^{2+}$ and $^{27}Al^{3+}$ and therefore could not be measured.

An ultra-sensitive (10^{-12} g of Be) mass spectrographic technique, based on the formation of Be ion emission from a tungsten filament coated with the sample, was developed by McHugh and Sheffiend (ref. 56). Although very sensitive, the technique lacked analytical precision and the time required for preparing samples limits the application to very special situations.

Relatively high sensitivity (submicrogram quantities) for beryllium, as metal chelates, has been attained by specialized mass spectrographic techniques. Majer, et al. (ref. 57) measured beryllium as the oxinate; Pagel, et al. (ref. 58) used beryllium β-diketonates; and Hughes, et al. (ref. 59) detected beryllium as the hexafluoroacetylacetonate. (Note - A potential interference from the $^{27}Al^{3+}$-ligand can also occur.) Although highly sensitive, the methods are not suitable for continuous or short-term intermittent monitoring because of the time required for derivative formation.

5. RECOMMENDED ANALYTICAL TECHNIQUE FOR CONTINUOUS MONITORING OF BERYLLIUM AND CADMIUM

There is no method available at this time that can be immediately adapted to monitoring particulate and/or fume emission from stationary sources for beryllium and/or cadmium on a continuous, round-the-clock basis. The work of Webb, et al. (see Section 4.1.1) suggests that a continuous monitor can be developed based on emission spectroscopic measurements of a continuous flowing (40 l/min.) stream of stack gases. This type of emission spectroscopic measurement can provide a means of monitoring both beryllium and cadmium (or most other metallic elements and some non-metals) simultaneously. The technique has the necessary (a) selectivity, (b) speed (30 sec.) for rapid, repeated analyses, and (c) sensitivity (∿1 $\mu g/m^3$).

An evaluation of the Webb-type emission spectrographic approach must be made to establish the efficiency of the excitation process when analyzing entrained particulate of variable particle size and when measuring stack emissions having moderate to high loadings of entrained particulate. The Webb system worked well in monitoring the beryllium content in a work environment where the particulate was principally beryllium compounds. No data are available regarding performance in measuring small amounts (1-100 ppm) of Be or Cd in inorganic particulate, e.g., fly ash.

Electrode wear and deposition of particulate from stack gases having high loadings of particulate may be major problems in applying the Webb technique to monitoring stack emissions. By using an electrodeless discharge system (radio-frequency coupled excitation), the electrode wear and deposition problems could be eliminated or minimized.

The major problem related to using radio-frequency excitation is the difficulty in initiating and maintaining an air plasma of desirable geometry. Also, adverse oxidation effects may limit the sensitivity. By blending mixtures of inert matrix gas (A or He), with air containing entrained particulate and with a reducing gas, e.g., hydrogen, a stable plasma and suitable sensitivity may be attained. However, by diluting the sample with an inert or a reducing gas, some loss in the capability to detect the lower concentrations of Be or Cd will be experienced.

A trade-off of performance specifications may depend on the type of emission source being tested. The Webb system may be usable for low (1-100 $\mu g/m^3$) Be or Cd levels in source emissions composed of particulate or fume having Be or Cd as major components and little, if any, other metallic elements. Similarly, the method based on the $^9Be(\alpha,n,\gamma)^{12}C$ reaction (see Section 4.4.5) can be used for measuring beryllium continuously in atmospheres or stack gas emissions containing principally beryllium or its compounds down to 1 $\mu g/m^3$, but cannot be used where non-beryllium particulate would be excessive.

X-ray fluorescence techniques can be used for measuring cadmium, but not for determining beryllium. X-ray tube excitation sources have been applied to analyses for cadmium, but limited work has been performed with radioisotope induced x-ray emission (^{241}Am). The application of radioisotope induced x-ray emission spectroscopy to determining cadmium in collected stack emission particulate may require further development of new or modified radioisotope sources, e.g., ^{125}I.

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APPENDIX III

BRIEFING DOCUMENT - ANALYTICAL TECHNIQUES FOR MERCURY

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ANALYTICAL TECHNOLOGY FOR CONTINUOUS MONITORING OF STATIONARY SOURCE EMISSIONS FOR MERCURY

1. INTRODUCTION

Mercury in the atmosphere can exist in many chemical and physical forms depending on the type of source emission. Elemental mercury, because of its high vapor pressure, is constantly emitted by many industries as vapor. Chemically bound mercury - organic and inorganic compounds - can be emitted as vapor or aerosols. The volatile elemental mercury is readily produced by thermal decomposition of chemically bound mercury at relatively moderate temperatures and by a combination of reduction and disproportionation reactions.

Continuous monitoring of stationary source emissions for mercury must be able to handle vapor and particulate, either of which could be elemental mercury, inorganic or organic mercurials, or mercury (or its compounds) adsorbed on particulate.

At this time, there is no method that has been sufficiently tested or used for continuous monitoring of total mercury emissions from stationary sources.

2. SOURCES AND TYPE OF EMISSION

Emission sources and uses were identified in a survey by Stahl (ref. 1). These include ore refining, electrical apparatus, electrolytic production of chlorine and caustic soda, paints, pharmaceuticals, agricultural compounds, power plants, and incinerators. The principal chemical forms are classified as elemental mercury, mercuric oxides, inorganic and alkyl mercury salts (nitrates, sulfates, chlorides, sulfides, fluorides, bromides, iodides) and organo-mercury compounds (alkyl or aryl mercury compounds or salts of organic acids). Most of these compounds are volatile or decompose into elemental mercury at moderate temperatures.

Mercuric oxide (500°C), mercuric oxychloride (260°C), mercuric iodide (290-310°C) mercuric fluoride (645°C), mercuric bromide (130-140°C), and mercurous nitrite (100°C) decompose, yielding principally volatile, elemental mercury (b.p. 356.6°C). Other inorganic salts, mercurous chloride (400°C), mercurous bromide (345°C), mercurous iodide (140°C), and mercuric sulfide (584°C) sublime at low to moderate temperatures yielding vapor containing the individual molecular species, or a mixture containing elemental mercury, the original mercury compound, and a mercury compound in a higher oxidation state. The mixture can be obtained for moist compounds, whereas dry materials do not yield measurable amounts of the disproportionation products. If not dry, mercurous chloride decomposes at the sublimation temperature into Hg° and $HgCl_2$. There is also some evidence for a similar effect during sublimation of mercurous iodide (ref. 2).

Mercurous chloride has a vapor pressure of 0.004 mm @ 90°C and 0.27 mm @ 170°C. Mercuric chloride volatilizes rapidly at its melting point of 276°C and has a vapor pressure of 0.003 mm @ 60°C and 3 mm @ 152°C. The vapor pressure of mercuric bromide is reported as 0.045 mm @ 90°C and 3 mm @ 162°C (ref. 2).

Organo-mercury compounds are moderately volatile to highly volatile. Dimethylmercury has a normal boiling point of 95°C. Although no specific boiling point is given, methylmercuric chloride is reported as volatile at 100°C. Diphenylmercury sublimes at 121.8°C and phenylmercuric hydroxide decomposes at 200°C.

3. CANDIDATE ANALYTICAL TECHNIQUES

Methods of analyses for total mercury in various media have been based on colorimetry, emission or absorption spectroscopy, neutron activation analysis, x-ray fluorescence, isotope dilution and electrolysis (ref. 1). Some of the methods - colorimetry, neutron activation, and electrolysis - require considerable sample pretreatment and as a consequence cannot be readily adapted for continuous or intermittent, but rapid, monitoring systems. Many of the techniques require the collection of mercury and mercury compounds prior to analysis. In certain methods, for example, neutron activation, some sample separation is required before the mercury can be measured.

The high selectivity, sensitivity, and speed of the spectroscopic techniques make methods based on these principles most attractive. Several methods using the photometric measurement of the absorption of ultra-violet radiation at 2537 Å have formed the basis of commercial monitoring detectors for mercury vapor. The lower detection limit of these instruments is approximately 5 to 10 $\mu g/m^3$ but the instruments are subject to interference from chemical compounds, dust, and smoke which would absorb or scatter light at 2537 Å. To lower the detection limits of the photometers, techniques have been devised to concentrate the mercury vapor and/or eliminate the interferences. Other techniques using emission spectroscopic principles are very sensitive and have potential for a continuous or intermittent, but rapid, monitoring system.

This document describes the analytical approaches for direct, continuous monitoring of mercury vapor and/or mercury containing particulate. An attempt is made to show the advantages and limitations of each method.

Also, the means for collecting or concentrating the mercury specimen are described for possible use in short-term, intermittent monitoring requiring high sensitivity.

The analytical methodology is categorized as (a) Mercury Vapor Photometers and Flameless Atomic Absorption, (b) Flame Atomic Absorption and Fluorescence Spectrophotometry, (3) Emission Spectroscopy, (d) Formation of Colored Complexes, (e) Neutron Activation Analysis, (f) Radioisotopic Method, (g) Argon Ionization Detection, and (h) Condensation Nuclei Monitor.

3.1 Mercury Vapor Photometers and Flameless Atomic Absorption Spectrometry

The mercury vapor photometer and flameless atomic absorption spectrophotometry are based on the principle that mercury resonance radiation at a wavelength of 2537 Å is strongly absorbed by mercury vapor. Both techniques measure the atomic absorption phenomena.

In the simpler mercury vapor photometer, generally no monochromator is used and the source of the mercury resonance radiation is a low pressure germicidal lamp. Isolation of the 2537 Å line is accomplished with a narrow-band photoelectric cell. The flameless atomic absorption spectrophotometer uses a hollow cathode lamp as an energy source and a monochromator to isolate the 2537 Å line. The monochromator minimizes spectral interference, principally stray radiation due to (a) ambient radiation, (b) reflected radiation from the exciting source, and (c) fluorescence of the silica cell components excited by UV radiation. Stray radiation causes nonlinear or reduction of photometric response which is characterized by curvature and reduction in slope of the analytical calibration curves.

A number of low cost, portable, continuous, mercury-vapor photometers are available commercially (Coleman Instruments; Beckman Instruments, Inc.). The basic design was developed by Woodson (ref. 3). Many other variations have been reported (ref. 4-17). When used as a direct measuring device without pre-concentration steps, the lower sensitivity is in the range of 5 to 10 $\mu g/m^3$. Costs range from $300 to $1000 (without recorder) and the devices are approximately 13" x 12" x 8" and weigh between 14 to 20 lbs.

Flameless atomic absorption spectrophotometers are generally more sensitive, but are also more expensive, ranging from $2500 to approximately $10,000 (without recorder), and weigh approximately 150 lbs.

Although these techniques are continuous monitors and are very sensitive, considerable interferences can occur which affect the reliability of the measurements. Dust, smoke, and fog can reduce the light intensity and magnetic interferences are reported. A number of compounds, Table I (ref. 17), also absorb ultraviolet radiation at 2537 Å and could result in erroneous high mercury values. As shown in Table I, the spectral response for mercury vapor is much greater than the responses for equivalent amounts of the potential interfering compounds. Relatively high concentrations of these compounds are required before interference becomes a problem.

Olin Corporation markets an automatic "Mercury Monitor for Gases" based on pyrolysis (760°C) of total mercury containing materials - metallic, ionic, organic - followed by reduction with stannous chloride in hydrochloric acid solution to yield elemental mercury vapor. The mercury vapor content is measured in an ultraviolet spectrophotometer equipped with a one meter gas cell. A working concentration range of 0-0.05 mg/m^3 or higher in air or other gaseous systems is quoted by the manufacturer. No data on the specific, lower detection limit is given. The analysis cycle is approximately six minutes per analysis. The instrument cost is quoted as approximately $20,000.

Various methods have been devised to prevent or compensate for interferences. Although developed principally for measuring mercury in occupational environments, the techniques in modified form can also be used to monitor mercury from stationary source emissions. Background compensation with a deuterium continuum lamp, broadened emission line, twin cells and mercury removal, Zeeman effect, and amalgamation on silver, gold or palladium have been used. Technology relating to some of these methods are presented in the following subsections.

Table I

SENSITIVITY OF MERCURY VAPOR PHOTOMETER

	Relative Sensitivity (ppm)
Mercury	0.0001
Tetraethyllead	0.13
Xylene	0.2
Monochlorobenzene	0.3
Aniline	0.3
Perchloroethylene	0.5
Chloroprene	0.5
Toluene	1.0
Benzene	1.2
Vinylacetylene	1.6
Phosgene	5
Acetone	5
Ethylbenzene	5
Pentachloroethane	7
Hydrogen sulfide	8
Trichloroethylene	10
Carbon disulfide	12
Gasoline (Blue Sunoco)	50

Photometer Insensitive to:

Methylene chloride
Carbon tetrachloride
Ethylene dichloride
Tetrachloroethane
Chloroform
Methyl chloride
Vinyl chloride
Methyl alcohol
Ethyl alcohol
Amyl alcohol
Ethyl acetate
Ethyl Cellosolve
Methyl Cellosolve
Dowtherm A
Water vapor

3.1.1 Mercury Photometric Analysis Using a Source with a Broadened Emission Line to Minimize Interferences

3.1.1.1 Principle and Applicability

3.1.1.1.1 Principle - Mercury vapor in air atmospheres is measured quantitatively with a photometric analyzer which measures the absorption of a broadened emission line (at 2537 Å) emitted by a mercury vapor lamp. The width of the emission line is greater than the width of the absorption line. The portion of the broadened emission line that is outside the absorption line of the mercury vapor in the sample is not absorbed by the mercury vapor. This portion of the emission line is used as a reference to account for the absorption of non-mercury species which normally interfere with the mercury photometric measurements.

High sensitivity is attained by using a folded path concept based on four internal reflections of the 2537 Å mercury line in the sample cell.

3.1.1.1.2 Applicability - System was designed for measuring mercury emitted from solid or liquid batch samples.

Method can be used for intermittent, but rapid, monitoring of mercury vapor in atmospheric samples or for measuring mercury vapor emitted from mercury-containing specimens which yield elemental mercury on pretreatment with thermal or chemical reduction. Spectral interferences common to the mercury photometric measurement are minimized.

3.1.1.2 Range and Sensitivity

No data given, but should be able to detect at least 5 $\mu g/m^3$.

3.1.1.3 Interferences

Compensation technique used in measuring sidebands of the broadened emission line from the mercury vapor lamp should correct for most, if not all, interferences (dust, aromatic hydrocarbons, etc.) encountered in the application of the mercury vapor photometers.

3.1.1.4 Accuracy, Precision and Stability

No data given.

3.1.1.5 Apparatus

3.1.1.5.1 Mercury Vapor Lamp - Model 11SC1 (Penray Ultraviolet Products) with emission line at 2537 Å having a linewidth of about 0.1 Å.

3.1.1.5.2 Sample Cell - Plane and spherical mirrors are used internally to provide four reflections.

3.1.1.5.3 Interference Filter - To isolate 2537 Å emission.

3.1.1.5.4 Optical Filter - Cylindrical cell constructed with quartz windows and containing dense mercury vapor. Cell is used to absorb or suppress the central portion of the emission line, so that the light passing through the optical filter is contained within the sidebands only.

3.1.1.5.5 Source and Reference Photomultipliers - RCA 1P28.

3.1.1.5.6 Electronics - Preamplifiers, differential amplifier, integrator, power supplies, and scaler and readout meter.

3.1.1.5.7 Flow Controller - 4 liters/minute.

3.1.1.5.8 Dilution Apparatus - To provide mercury sample for calibration.

3.1.1.6 Time Cycle for Sampling and Measuring

No data given, but should be very rapid. Time cycle is dependent mostly on the ease by which the elemental mercury can be obtained in the thermal decomposition step. A sampling time estimate would be approximately 5-10 minutes.

3.1.1.7 Calibration Procedure

Special dilution apparatus is provided in which mercury vapor can be diluted with air.

3.1.1.8 Method of Sampling and Sample Preparation

Batch samples (solid or liquid) were heated to vaporize elemental mercury into a stream of purified air which was passed through the analyzer.

3.1.1.9 Multi-element Application

Present system is specific for mercury, but the principle used could be applied with hardware modifications to other volatile elements.

3.1.1.10 Physical Dimensions

None reported; probably small to moderate in size. Estimated 4' x 2' x 4'.

3.1.1.11 Unit Output

Weight units or concentration units.

3.1.1.12 Safety Hazard

Moderate electrical voltages.

3.1.1.13 Recommendation for Method Improvement

System was designed principally for measuring mercury in batch samples. Minor modifications would permit continuous or semi-continuous measurement of air specimens. The deterioration of the mirrored surfaces in the sample cell could become a major problem if air or stack emission samples had high loadings of particulate. Elimination of the mirrors and the use of a long optical path may provide sufficient sensitivity with moderate loadings of particulate.

Instrument response factors would have to be determined tc establish higher flow rates than 4 liters/minute if direct stack emissions were to be analyzed.

3.1.1.14 References

Barringer, A. R., "Method for Absorption Analysis Using a Source Having a Broadened Emission Line," U.S. 3,571,589 (23 March 1971).

Barringer, A. R., "Interference-free Spectrometer for High-sensitivity Mercury Analyses of Soils, Rocks and Air," Trans. Inst. Mining & Metallurgy Sec. B, 75, Bull. 714, 120-4 (1966).

3.1.2 Mercury Photometric Analysis with Twin Cell System to Minimize Interferences

3.1.2.1 Principle and Applicability

3.1.2.1.1 Principle - Mercury vapor in air is measured by a photometric analyzer based on the absorption by the mercury vapor of radiation (2537 Å) emitted by a fused silica, low-pressure mercury vapor lamp. Fluctuations in lamp intensity and signal voltage are minimized by compensating with a reference path and separate detector in a twin-cell arrangement. Corrections for components, other than mercury, which also absorb at 2537 Å are accomplished by measuring the absorption background for a "demercurified" specimen simultaneously with a measurement on the mercury-containing air sample. Removal of mercury is attained by passing one-half of the sample through a column of glass wool impregnated with palladium chloride.

3.1.2.1.2 Applicability - Although designed for geochemical prospecting, the system can be used for direct measurement of mercury vapor in air, as well as mercury in solid samples - rocks and soils. Analyses on rocks and soils are performed on vapors generated by heating the samples to 600-800°C.

3.1.2.2 Range and Sensitivity

3.1.2.2.1 Range - No details on upper limits.

3.1.2.2.2 Sensitivity - Present instrument 10^{-4} μg Hg with possibility of 10^{-5} μg Hg.

3.1.2.3 Interferences

3.1.2.3.1 Chemical and Spectral - The effects of ultraviolet absorbing materials (organic compounds, ozone, etc.) are minimized or eliminated by using the twin cell arrangement with a reference path containing the air sample with mercury removed. (Note - The reaction of Hg with $PdCl_2$ is specific and takes place spontaneously in the cold and in the absence of moisture.)

In addition, the generation of ozone from atmospheric oxygen by radiation having wavelengths <2000 Å emitted by the mercury lamp is eliminated by using a lamp made of slightly impure fused silica (Vycor) which filters out the undesirable radiation.

3.1.2.3.2 Physical - Physical scatter of ultraviolet radiation by fume, dust, and other suspensions in the vapor is compensated by employing the twin-cell reference path system.

Adsorption of mercury on glass, silica gel, and other materials in the instrument can be a problem. Degree of adsorption seems to be affected by the presence or absence of moisture. (Note - The effect is presented in Ref. 1, Section 3.1.2.14 as a private communication from S. H. Williston, but no data are given regarding whether the adsorption is enhanced or decreased by increasing moisture content.)

3.1.2.4 Accuracy, Precision and Stability

No data given for vapor, but a reproducibility of ±15% at the 95% confidence level over the range 1-10 ppm was reported for solid samples heated to 600-800°C.

3.1.2.5 Apparatus

3.1.2.5.1 Source - Low-pressure, fused-silica (Vycor) mercury vapor lamp.

3.1.2.5.2 Detector - Two photocells and suitable electrical circuit for measuring differential output.

3.1.2.5.3 Sample Cell - Two glass columns with quartz windows.

3.1.2.5.4 "Demercurifying" Agent - Palladium chloride, prepared by evaporating a 1% aqueous solution of $PdCl_2$ on glass wool. (Note - Apparently removes mercury from dry air down to concentrations below 0.01 $\mu g/m^3$ Hg).

3.1.2.5.5 Ancillary Equipment - Silica gel column to remove water vapor; flowmeters, glass wool; vacuum pump; meter or recorder; suitable valves and tubing; and electronic amplifiers.

3.1.2.6 Time Cycle for Sampling and Measuring

Analyses for mercury in air should be instantaneous and continuous.

No data are given for heating times required to release mercury from soil or rock samples. Estimated times are dependent on the method of introducing the sample into the hot zone, but could range from 1 to 15 minutes.

3.1.2.7 Calibration Procedure

Apparatus was calibrated by injecting known volumes of air saturated with mercury at different temperatures.

3.1.2.8 Method of Sampling and Sample Preparation

Air sampling was accomplished by drawing an air specimen through the instrument with a suction pump.

For solid materials, the mercury content is determined by heating (600-800°C) a known weight of sample and allowing the vapor to pass into the instrument as done for air sampling.

3.1.2.9 Multi-element Application

Method is specific for mercury.

3.1.2.10 Physical Dimensions

No data given, but unit is mobile and was designed for geochemical prospecting.

3.1.2.11 Unit Output

Voltage readings convertible to μg Hg or $\mu g/m^3$.

3.1.2.12 Safety Hazard

Moderate electrical voltages.

3.1.2.13 Recommendation for Method Improvement

The adsorption of mercury on glass and materials of construction in the presence of water must be evaluated.

By performing direct heating (∿800°C) of airborne particulate in moderate flowing air streams, an analyzer which measured total mercury (particulate and vapor) and/or mercury vapor can be developed. The major concern would be the residence time in the heated zone required to efficiently volatilize the mercury in the particulate. Flow rate limits have not been defined, but thermal decomposition of organo-mercury and inorganic mercury compounds has been accomplished in a continuous flow system at 5 liters/minute at 800°C (see ref. Leong and Ong below).

3.1.2.14 References

James, C. H. and J. S. Webb, "Sensitive Mercury Vapour Meter for Use in Geochemical Prospecting," Bull. Inst. Mining Met. 691 (6), 633-641 (1964).

Leong, P. C. and H. P. Ong, "Determination of Mercury by Using a Gold Trap in Samples Containing Considerable Sulfide Minerals," Anal. Chem. 43, 940-941 (1971).

3.1.3 Measurement of Mercury Vapor Using a Photometric System with a Mercury Resonance Lamp as a Monochromatic Source

3.1.3.1 Principle and Applicability

3.1.3.1.1 Principle - By coupling polychromatic radiation from a standard low pressure arc lamp through a highly evacuated (0.001-mm pressure) fused silica mercury resonance lamp, monochromatic radiation can be obtained. The resonance lamp will emit resonance radiations 1850 Å and 2537 Å. Since the radiation at 1850 Å will be absorbed by oxygen, pure 2537 Å radiation will be obtained. The line width (about 0.002 Å) is determined by Doppler's effect only and is a constant, irrespective of the line width of the exciting source.

With the resonance lamp system, no filters or narrow band pass photoelectric detectors are necessary as required in the standard mercury vapor photometer, and the monochromator, normally used with atomic absorption spectroscopy, is not needed. A highly sensitive mercury photometer, in which ultimate spectral sensitivity can be achieved, is possible.

3.1.3.1.2 Applicability - The system can be used in all applications in which the standard mercury vapor photometer is used. Disadvantages, such as (a) lamp instability due to temperature variations in low pressure arc discharges, (b) broadened and self-reversed emission lines, (c) reductions in spectral intensity and non-linearity of response resulting from use of filter or narrow band pass detectors, which are normally encountered with standard mercury photometers are eliminated.

Because of its high sensitivity, the technique can be used to measure mercury vapor regenerated by heat after it has been extracted by a collector - cadmium sulfide-impregnated asbestos, gold leaf, palladium chloride, etc.

3.1.3.2 Range and Sensitivity

3.1.3.2.1 Range - 0.0003 μg to 0.05 μg.

3.1.3.2.2 Sensitivity - 0.0003 μg.

3.1.3.3 Interferences

3.1.3.3.1 Chemical - Organic compounds and ozone, which also absorb radiation at 2537 Å, can interfere with detection of mercury vapor. To eliminate or compensate for these nonatomic interferences, a modification of the mercury photometer concept incorporating a resonance lamp filled with argon to provide a broadened resonance line was devised. (Ref.-See Section 3.1.3.14.)

A shutter is used to pass radiation from twin sources through two pathways. Path 1 is a four-stage system having (1) a resonance lamp filled with argon at one atmosphere pressure, (2) a cell filled with nitrogen at one atmosphere and containing a drop of mercury, (3) a low pressure resonance lamp containing mercury vapor at low pressure (0.001 mm), and (4) the sample absorption cell. Path 1 transmits a broadened resonance line, which measures only nonatomic absorption, while path 2 transmits the sharp resonance line, which measures both nonatomic and atomic absorption. The difference (atomic absorption) between the two values is relatable to the mercury vapor content in the sample.

3.1.3.3.2 Physical - Dust, smoke, and fog can interfere with the measurement by attenuating the transmission of radiation. Corrections can be made by using the system and techniques cited in sub-section 3.1.3.3.1.

Optical systems of the type used in this study, which do not use a dispersion device (spectrograph), are subject to problems (undesirable curvature and reduction in slope of the analytical response curves) caused by the presence of stray radiation. The four sources of stray radiation are:

1. Ambient radiation.
2. Reflected radiation from the exciting source.
3. Fluorescence of the fused silica excited by UV radiation.
4. Fluorescence of mercury vapor in the resonance lamp.

A detailed, quantitative examination of the stray radiation was performed (see reference below) and a system to minimize the effect was devised. By using a short (3 cm) focal length "suprasil" lens between the source and the resonance lamp, and by mounting a Wratten 18B filter as a window on the photomultiplier end of the absorption tube, the stray radiation was reduced to about 0.7%.

3.1.3.4 Accuracy, Precision and Stability

The percent standard deviation at 0.0003 μg is 37% and 2.9-7.7% in the range 0.01 μg to 0.04 μg.

Long term stability was affected by the purity of the gas in the resonance lamp. Small amounts of foreign components, e.g., H_2 and CO_2 can cause quenching of the resonance radiation. Deterioration of the re-emitted energy occurred when an adhesive was used to cement the parts of the lamp. However, when the lamp was constructed by fusing components together, no loss of energy occurred.

3.1.3.5 Apparatus

3.1.3.5.1 Excitation Source - G.E. ozone lamp GE OZ 4511 (selected for high stability).

3.1.3.5.2 Mercury Resonance Lamp - Highly evacuated fused silica containing mercury vapor (∿0.001 mm) at room temperature.

3.1.3.5.3 Absorption Cell - Tube 1 cm diameter x 35 cm length fitted with two windows, one of fused silica at the resonance lamp end, while the other, made of Wratten 18B glass filter, is placed at the detector end. (Note - The filter cuts off the visible "stray" radiation produced by fluorescence of the fused silica excited by UV radiation and fluorescence of mercury vapor in the resonance lamp.)

3.1.3.5.4 Photodetector - RCA 1P28 photomultipliers (matched) enclosed in light-proof housing to exclude ambient radiation.

3.1.3.5.5 Ancillary Equipment - Vacuum pump, tubing, flowmeters, amplifiers and recorder, lens, collimator.

3.1.3.6 Time Cycle for Sampling and Measuring

Two types of operational modes are possible: (a) continuous operation and instantaneous response of air samples, and (b) batch analyses on "collected" mercury samples.

3.1.3.7 Calibration Procedure

A calibration curve was obtained with mercury content ranging from 0.01-0.05 μg. Known quantities of mercury, as the sulfide, were added to a sample tube which could be vented into the absorption cell to permit diffusion of mercury into the optical path.

The sulfide mercury solution was prepared from mercuric chloride solution to which was added a solution of hydrated sodium sulfide. Suitable volumes of the solution were introduced into sample tubes. After evaporation to dryness in a desiccator under reduced pressure, the tubes were connected to the absorption cell and heated to ∿100°C with an infrared lamp to promote diffusion of mercury into the cell.

3.1.3.8 Method of Sampling and Sample Preparation

Two modes are possible: (a) Continuous sampling and measurement of mercury and air samples taken directly; and (b) collection of mercury by cadmium sulfide impregnated asbestos, gold leaf, palladium chloride, etc., followed by thermal regeneration of mercury vapor into the photometer.

3.1.3.9 Multi-element Application

Technique designed specifically for mercury, although general principles could be adapted to other volatile elements.

3.1.3.10 Physical Dimensions

None reported other than a statement that the instrument is compact and can be powered with batteries to allow for portable operation.

3.1.3.11 Unit Output

Micrograms/m^3 or mass units.

3.1.3.12 Safety Hazard

Moderate electrical voltages; some ozone generation.

3.1.3.13 Recommendation for Method Improvement

Tandem coupling to a thermal decomposition furnace should be considered to permit analyses of organo-mercurials and possibly mercury-containing particulate.

3.1.3.14 Reference

Ling, C., "Sensitive Simple Mercury Photometer Using Mercury Resonance Lamp as a Monochromatic Source," Anal. Chem. 39, 798-804 (1967).

3.1.4 Analyses for Mercury: Photometric Measurements Corrected with Zeeman Effect

3.1.4.1 Principle and Applicability

3.1 4.1.1 Principle - Mercury, free or chemically bound, is vaporized in air or oxygen in an absorption cell heated externally by a furnace. The quantity of mercury vapor generated is measured with a mercury photometer.

To compensate for non-mercury components which either scatter or absorb the 2537 Å radiation, the radiation from the excitation source (electrodeless ^{199}Hg lamp) is broadened by applying a magnetic field (10 kgauss) to the source. The broadening results from hyperfine splitting (Zeeman effect) of the 2537 Å line. By using an argon filled cell containing mercury vapor after the furnace and before the detector to absorb only the center component of the broadened 2537 Å, a comparison measurement can be performed which compensates for non-mercury absorption. The non-mercury absorption is established from absorption of the two components created by the Zeeman effect, which lie above and below the 2537 Å line.

3.1.4.1.2 Applicability - System was applied to analyzing for mercury in food, but can be used on any system for measuring mercury vapor. Bound mercury must be decomposed into element mercury vapor. Although the system was not designed for continuous monitoring of air, suitable modifications can be made to permit this type of measurement. The major problem, as with any mercury photometer measurement for continuous monitoring, is the efficiency of the decomposition process to form elemental mercury vapor from bound-mercury.

3.1.4.2 Range and Sensitivity

No details are given other than detection of 0.04 ppm in food samples.

3.1.4.3 Interferences

System is designed to compensate for interferences which normally affect the mercury photometric measurement. Could not be used in region of high magnetic field.

3.1.4.4 Accuracy, Precision, and Stability

Little data reported. For tuna containing 0.49 and 0.24 ppm of Hg, all measurements were within 12% of the average over the range 5 to 35 ng of Hg.

3.1.4.4 Apparatus

3.1.4.5.1 Excitation source - Electrodeless ^{199}Hg lamp.

3.1.4.5.2 10 kgauss permanent magnet.

3.1.4.5.3 Absorption cell and automatic heating furnace (up to 500°C).

3.1.4.5.4 2537 Å filter.

3.1.4.5.5 Natural Hg cell filled with argon.

3.1.4.5.6 Detection system - photomultipliers, phase-sensitive detector and digital integrator.

3.1.4.6 Time Cycle for Sampling and Measuring

Total time cycle is approximately one minute.

3.1.4.7 Calibration Procedure

Standards were prepared by mixing HgI in carbon and HgO in carbon and starch.

3.1.4.8 Method of Sampling and Sample Preparation

Known weights of sample were introduced into the furnace. No chemical pretreatment is necessary.

3.1.4.9 Multi-element Application

Potentially could be applied to any element currently measured by atomic absorption techniques.

3.1.4.10 Physical Dimension

No data reported. Basic photometer and furnace should be relatively small. The weight of the magnet, which is unknown, could be significant.

3.1.4.11 Unit Output

Nanograms of Hg.

3.1.4.12 Safety Hazard

Moderate voltages in electronics.

3.1.4.13 Recommendations for Method Improvement

Although not designed for continuous monitoring of air or stack gases, the decomposition step could be suitably modified to provide continuous decomposition. Again, as with any monitor based on photometric measurement of mercury vapor, the key factor is the efficiency of the decomposition step.

3.1.4.14 Reference

Hadeishi, T., and R. D. McLaughlin, "Hyperfine Zeeman Effect Atomic Absorption Spectrometer for Mercury," Science, 174, 404-407 (1971).

3.1.5 Mercury Photometric Analysis with Thermal Decomposition and Gold Concentrator

3.1.5.1 Principle and Applicability

3.1.5.1.1 Principle - Method was devised for measuring mercury in geologic materials, but principles can be adapted to monitoring particulate in stack emissions. Geologic materials are heated to 800°C or 900°C in an induction furnace (ref. 1) or with 400-kilocycle radio-frequency at 500°C (ref. 2) to decompose mercury-containing particulate and organo-mercury compounds. Mercury vapor, released during the decomposition, is collected from air at 28- liters/minute on gold wool (ref. 1) or gold foil (ref. 2) at room temperature or 215-255°C as potential interfering compounds and smoke are exhausted. Mercury is subsequently desorbed from the gold amalgamator by using radio-frequency induction heating to rapidly heat the amalgam to 800-850°C. Mercury vapor content was measured by absorption of radiation at 2537 Å.

3.1.5.1.2 Applicability - Technique was developed for measuring mercury in soils, rocks, and gas on a batch sample basis. Consideration should be given to the potential adaptation to intermittent, but short time cycle, analyses on stack emissions. These analyses would be performed on mercury vapor generated by an induction (or resistance) furnace or an electrodeless radio-frequency induced plasma used to heat stack effluent on a continuous basis. The major concern is the efficiency of the decomposition process, which would be dependent on the temperature of the decomposition zone, particle size, stability of the mercury-containing compound, and residence time of mercury compound in the decomposition zone.

3.1.5.2 Range and Sensitivity

3.1.5.2.1 Range - 1×10^{-9}g to $>300 \times 10^{-9}$g.

3.1.5.2.2 Sensitivity - Detection limit reported as 1×10^{-9}g with low cost mercury vapor meter, but has potential to detect 1×10^{-12}g.

3.1.5.3 Interferences

Use of gold to collect the mercury vapor permits removal of organic vapors, sulfur contaminants, and particulate which could interfere with the mercury photometric analyzer. In cases where tars and water can condense on the gold and thus lessen its effect as an amalgam, operation of the gold collector between 25° and 259°C may be required to eliminate condensation.

During measurements on samples of galena and sphalerite, minor amounts of lead and zinc oxides were deposited on the tube adjoining the furnace and gold collector. The build-up of deposits of this type must be considered in the design criteria and could be a major maintenance problem in continuous, long-term use.

Some deterioration of the desorption efficiency (lengthening of desorption time by several seconds) is reported with long term use of gold wool. Also, when amalgamation was performed at room temperature, 3 to 6% of the mercury was retained on the gold wool, whereas less than 2% was retained at temperatures ranging from 215-255°C.

3.1.5.4 Accuracy, Precision and Stability

Accuracy was assessed by comparing the measured mercury contents with spectrographic analyses of rock specimens and was reported as 5-10% of the amount present depending on the level.

Reproducibility of the method was determined by analyzing a standard rock sample ten times and was reported as 11% deviation from the mean.

Although some deterioration of the gold amalgam efficiency was noted, several hundred analyses of geological specimens were performed with reliable results.

3.1.5.5 Apparatus

3.1.5.5.1 Decomposition System - Induction furnace - Leco Model 521-500 or unidentified resistance furnace (ref. 1); 400-kilocycle radio-frequency induction heater (ref. 2); quartz chamber.

3.1.5.5.2 Gold Collector - (a) 300 ft of gold (99.99% Au) wire of 0.003-in. diameter with a theoretical surface of 34 in.^{2} (ref. 1); (b) 15 g of gold squares (2 mm x 2 mm x 1/2 mm).

3.1.5.5.3 Gold Collector Desorption System - Induction furnace - Leco Model 521-500 at 800-900°C (ref. 1); 400-kilocycle radio-frequency induction heater at 500-600°C (ref. 2).

3.1.5.5.4 Detector - Low cost mercury vapor photometer (unidentified) (ref. 1); specially designed single- or double-cavity absorption chamber with differential amplifier, voltage-frequency converter, electronic counter and timer (ref. 2).

3.1.5.6 Time Cycle for Sampling and Measurement

Approximately 4 to 8 minutes total time.

3.1.5.7 Calibration Procedure

Mercury from known volumes of air saturated with mercury was collected on the gold amalgam (ref. 1) and different weighed aliquots of a standard sample were analyzed (ref. 2).

3.1.5.8 Method of Sampling and Sample Preparation

Solids or gases were heated from 500-900°C for 1-2 minutes to vaporize mercury which was collected as a gold amalgam. Mercury concentrated as the gold amalgam was subsequently vaporized into a mercury vapor photometer. Note - Efficiency for forming an amalgam with gold and subsequent desorption of mercury was excellent, but much poorer desorption (∿50%) efficiency was observed with platinum.

3.1.5.9 Multi-element Application

Specific for mercury.

3.1.5.10 Physical Dimension

No data reported, but estimated as 4' x 2' x 6'.

3.1.5.11 Unit Output

Mass units (nanograms).

3.1.5.12 Safety Hazard

Normal electric voltages.

3.1.5.13 Recommendation for Method Improvement

Must determine efficiency of sample decomposition with induction heating or use of electrodeless radio-frequency plasma for continuous operation.

3.1.5.14 References

(1) Azzaris, L. M., "A Method of Determining Traces of Mercury in Geologic Materials," Can. Dept. Energy, Mines Resour.; Geol. Surv. Can., Pap. No. 66-54, pp. 13-26 (1967).

(2) Vaughn, W. W. and J. H. McCarthy, Jr., "An Instrumental Technique for the Determination of Submicrogram Concentrations of Mercury in Soils, Rocks, and Gas," Geological Survey Research, pp. D123-D127 (1964).

3.1.6 Photometric Analyses of Mercury Vapor - Detection and Estimation of Organo-Mercury Dusts and Vapors in the Atmosphere

3.1.6.1 Principle and Applicability

3.1.6.1.1 Principle - Total airborne mercury (organo and metallic) was determined by using thermal decomposition at 800°C of all mercury forms to elemental mercury followed by analysis with a mercury vapor photometer. (Note - Furnace vapor is cooled to atmospheric temperature before entering photometer.)

3.1.6.1.2 Applicability - System was designed to monitor mercury and organo-mercury fungicides in the atmosphere where seed treatment is carried out and where treated seed is stored in large quantities. Technique should be applicable in any organo-mercury or mercury vapor atmosphere where the total organic vapor does not exceed the combustion capacity of the decomposition tube. (Note - Excessive levels of hydrocarbons, dust, ozone, etc., can interfere with the photometric analysis. All organic material must be decomposed and oxidized prior to the photometric measurement.) There is not sufficient data to indicate the efficiency at which the system operates for decomposition and measurement of mercury-containing particulate.

Organo-mercury compounds are decomposed quantitatively at a temperature of 800°C and at a flow-rate of 5 liters/minute.

3.1.6.2 Range and Sensitivity

3.1.6.2.1 Range - 0-750 $\mu g/m^3$.

3.1.6.2.2 Sensitivity - Estimated as $<0.01\ \mu g/m^3$.

3.1.6.3 Interferences

3.1.6.3.1 Chemical - All organic contamination must be eliminated in the combustion process. The effect of ozone, generated by the mercury lamp, should be minimized by proper ventilation to limit accumulation of ozone in the source chamber. Interferences normally encountered in the mercury photometric measurements would also be expected in the read-out system of this procedure. (Ref.-See Section 3.1.6.14.)

3.1.6.3.2 Physical - Light scattering and attendant loss of radiation must be considered if the system is used in atmospheres of high dust loadings. The filter located after the furnace and prior to the photometric detector should minimize the scattering effect from particulate.

3.1.6.4 Accuracy, Precision and Stability

No data reported. Should have the same accuracy and precision as the general mercury vapor photometric systems.

3.1.6.5 Apparatus

3.1.6.5.1 Furnace - Tube furnace (Section 1A of CR300 - A. Gallenkamp & Co. Ltd.) with silica tube (1/2-in. bore, 20-in. length bent into U-tube of uneven length with longer arm of 10 in.).

3.1.6.5.2 Condenser - 5-in. double surface type.

3.1.6.5.3 Mercury Vapor Concentration Meter - Type E3472 (Hendry Relays Ltd).

3.1.6.5.4 Ancillary Equipment - Flowmeter, needle valve, filter, tubing, vacuum pump, pyrometer, thermocouple, energy regulator (220 V - 1,300 W), recorder (10 mv).

3.1.6.6 Time Cycle for Sampling and Measuring

Samples are taken and measured continuously and instantaneously.

3.1.6.7 Calibration Procedure

Calibration was performed by drawing a small flow of air (10 to 100 ml/min) over a metallic mercury reference held at a constant temperature until saturation of the air with mercury is achieved. This flow was diluted with additional air to reduce the mercury concentration to a measurable level at 25°C and at the same time increasing the air flow to the required rate of 5 liters/minute. These data were extrapolated back to a zero flow of air over the mercury, giving the concentration at saturation point. This was repeated at several fixed temperatures and the results were compared to published data by Jacobs (1949)[1], Lindstrom (1958)[2], and Handbook of Chemistry and Physics.

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[1] Jacobs, M. B., Analytical Chemistry of Industrial Poisons, 2nd Ed., p. 222 (London: Interscience) (1949).

[2] Lindstrom, O. J. Agric. Ed. Chem. 6, 283 (1958).

3.1.6.8 Method of Sampling and Sample Preparation

The air sample was drawn through the apparatus at 5 liters/minute. When the air flow was passed through the furnace, total mercury (organo and metallic) was determined. When the air flow bypassed the furnace, metallic mercury only was read and the organo-mercury was calculated by difference.

3.1.6.9 Multi-element Application

Technique, as designed, is specific for mercury. By using atomic absorption equipment, the concept of pretreating the sample in a tube furnace prior to absorption measurement could be adapted to other volatile organo-metallic compounds (e.g., lead).

3.1.6.10 Physical Dimensions

Height - 23 in.; width - 21 in.; depth - 12 in.; and weight - 88 lbs.

3.1.6.11 Unit Output

Micrograms/meter^3.

3.1.6.12 Safety Hazard

Moderate electrical voltages.

3.1.6.13 Recommendations for Method Improvement

The efficiency of the decomposition technique must be established for mercury-containing particulate before the system can be applied as an air pollution (universal) monitor for mercury.

The air flow rate (5 liters/minute) may be a limiting factor in an application to stack monitoring. Redesign of the instrument (higher temperatures and/or longer heated zone or double pass) may be necessary to attain sufficiently high decomposition efficiencies at higher flow rates.

Consideration should be given to maintaining the sample at warm to moderate temperatures after the furnace to insure against loss of mercury on the glass walls of the system after vapors pass into and through the cooling condenser.

3.1.6.14 Reference

Hamilton, G. A. and A. D. Ruthven, "An Apparatus for the Detection and Estimation of Organo-mercury Dusts and Vapours in the Atmosphere," Laboratory Practice 15, 995-997 (1966).

3.1.7 Portable Mercury Vapor Photometer

3.1.7.1 Principle and Applicability

3.1.7.1.1 Principle - Mercury vapor concentrations are determined by measuring change in ultraviolet radiation intensity resulting from the absorption of radiation at the mercury resonance line at 2536.5Å. The detection system responds to the difference in output voltages for dissimilar, but balanced phototubes. One of the phototubes responds only to visible radiation, whereas the other responds to both visible and ultraviolet radiation.

3.1.7.1.2 Applicability - System was designed as a self-contained survey meter for mercury vapor only. Weight and size factors permitted portability and battery power allows use in inaccessible sites.

Device is not directly applicable to stack monitoring, but with suitable modification the concept is attractive for a very low cost, stable, mercury vapor monitor.

The system would be subject to potential interferences from ultraviolet absorbing materials, but would compensate, in part, for scattering losses due to particulate. Potential interferences could be eliminated by using a mercury isolation-desorption step.

3.1.7.2 Range and Sensitivity

3.1.7.2.1 Range - 0.04 to 0.6 mg/m³.

3.1.7.2.2 Sensitivity - Detection limit estimated from calibration curves as approximately 0.02 to 0.04 mg/m³.

3.1.7.3 Interferences

3.1.7.3.1 Chemical - Organic compounds, ozone, and other materials which absorb ultraviolet radiation.

3.1.7.3.2 Physical - Radiation scatter effect resulting from particulate, etc., would be minimized by comparison of ultraviolet and visible radiation.

Magnetic field effects are minimized by housing amplifier tubes in a magnetic shield.

3.1.7.4 Accuracy, Precision and Stability

Instrument reproducibility at any mercury vapor concentration is 2% of full scale. Warm-up period of 20 minutes is required to minimize drift. After this period, the drift is less than one-and-a-half meter divisions per hour. The instrument requires minor zero adjustment with shift in ambient temperature.

Instrument was in operation for over 500 hours without serious malfunction. Only maintenance was the redistribution of mercury droplets in the mercury lamp.

3.1.7.5 Apparatus

3.1.7.5.1 Ultraviolet Absorption Cell - Flow-through chamber containing phototubes, UV source lamp, calibration filter, and light baffle.

3.1.7.5.2 Ultraviolet Light Source - GE B-H6 mercury discharge lamp selected for low current drain. Operating current of 0.75 milliampere provided adequate light intensity. Temperature effect on emission intensity and ratio of ultraviolet to visible emission was minimized by jacketing the source with a quartz envelope. The trapped air served as a thermal insulating medium. Although the warm-up time was increased, the zero shift due to changes in ambient temperature was reduced.

3.1.7.5.3 Detection System - A Type 934 phototube which responds only to light in the visible spectrum is used as a reference. A Type 935 which responds to light in both the visible and ultraviolet regions is used as a signal phototube. Metering circuit uses two balanced CK526AX subminiature tubes to amplify outputs of phototubes and to develop sufficient power to operate a 20-microampere meter. The CK525AX tubes were selected because of low filament and power requirements, ability to withstand mechanical shock without shift in response, and long term stability.

3.1.7.5.4 Sample Blower - Low power, battery operated (6V, 0.25 A) centrifugal blower operating at a flow rate of 0.5 cfm.

3.1.7.6 Time Cycle for Sampling and Measuring

For batch samples, sampling and measuring time is five seconds; flushing time is ten seconds.

3.1.7.7 Calibration Procedure

Instrument was calibrated with a mercury vapor generator (not identified). Field calibration is obtained by checking two points on the response curve. Instrument is adjusted for zero response with no mercury vapor present. (Note - Hopcalite filter used if necessary.) The second point, full scale, was provided by using a filter made of Pyrex glass which was inserted between lamp and signal detector to produce an output equivalent to 3.5 mg Hg/m^3 of air.

3.1.7.8 Method of Sampling and Sample Preparation

Blower pushed air through instrument at 0.5 ft^3/min. No sample pretreatment was used.

3.1.7.9 Multi-element Application

Designed specifically for mercury vapor.

3.1.7.10 Physical Dimensions

Weight - 18 lbs; size - occupies 0.3 ft^3.

3.1.7.11 Unit Output

Microamps convertible to mg/m^3.

3.1.7.12 Safety Hazard

None.

3.1.7.13 Recommendation for Method Improvement

Some form of compensation or sample treatment is needed to minimize effect of other ultraviolet absorbing species.

Placement of phototubes, lamp, and calibration filter in the absorption cell would be critical in a stream containing high loading of particulate. Separate optical and sample transport paths are needed. Problems with particulate deposition would also be encountered with the blower on the inlet side.

Concept could be modified for use as the detection subsystem in a thermal decomposition - Hg isolation and desorption - detection system for monitoring total Hg emission.

3.1.7.14 Reference

McMurray, C. S., and J. W. Redmond, "Portable Mercury Vapor Detector," Report No. Y-1188, Union Carbide Nuclear Company, Oak Ridge, Tennessee, Jan. 7, 1958.

3.2 Flame Atomic Absorption and Atomic Fluorescence Spectroscopy

Atomic absorption measurements of mercury with conventional flame techniques are relatively insensitive when compared to results from nonflame methods. Detection limits of 10 μg/ml of Hg in water with conventional flame techniques and 0.001 μg/ml of Hg in water with nonflame methods are common.

The principal problem with flame techniques is the unfavorable distribution of mercury in the Hg^{2+}, Hg^{1+} and Hg^0 states. Greater sensitivity is obtained for mercury (I) than for mercury(II), and further increase in sensitivity results when mercury(I) is reduced to elemental mercury (ref. 19). An advantage of the nonflame technique results from the fact that the sample is introduced into the optical path as elemental mercury (Hg^0).

Atomic fluorescence spectroscopy has been used to determine mercury in aqueous media (ref. 20-22). Elements which emit resonance lines in the UV (below 3000 Å) can be adapted readily to atomic fluorescence measurements. In addition, elements with resonance lines in the UV and with weak absorption (Hg 2537 Å) are particularly suited to atomic fluorescence flame spectrometry. This factor can produce a major advantage of atomic fluorescence over atomic absorption and is due principally to better quantum efficiencies (ref. 20-22). Improvements in sensitivity can reach a factor of 10 (0.08 μg/ml as compared to 0.8 μg/ml).

Additional enhancement of sensitivity and attendant lowering of the detection limit can be attained by using the reduction of Hg to metal during atomization (ref. 23). With the introduction of a reducing agent, $SnCl_2$, fluorescence intensity is increased by a factor of 100, permitting a detection level of 0.002 μg/ml at a confidence level of 95%. A number of elements and ions produce interferences. The S^{2-} ion must be absent; 50 μg Au, Pt, Cr(VI), and 0.5 mg Ag all in 1 ml interfere in the determination of 1 mg Hg/ml.

By using an interference filter with auxiliary optics of low *f*-number (ref. 24) or by using a solar-blind photomultiplier (ref. 25) in place of a conventional monochromator, nondispersive atomic fluorescence analyses for Hg, Zn and Cd in water are possible. For mercury, the limit of detection with the filter and photomultiplier is an order of magnitude lower than that obtained by using a monochromator (ref. 24). An optimum limit of detection of 2.5×10^{-4} μg/ml was obtained with the solar blind photomultiplier (ref. 24).

One of the more commonly accepted methods of monitoring ambient air for mercury is based on collecting free and bound mercury on activated carbon and desorbing mercury vapor with heat into the optical path of a flame atomic absorption unit. The advantages are: (a) concentration of mercury, (b) rapid desorption as vapor, (c) minimization of interferences, (d) conversion of all forms of mercury into elemental mercury, and (e) high sensitivity based on the concentration effect and desorption as a unit volume (or mass). Technology related to the collection on activated carbon and desorption into the atomic absorption flame is reported in the following subsection.

3.2.1 Determination of Mercury with Impregnated Charcoal and Flame Atomic Absorption Spectrophotometry

3.2.1.1 Principle and Applicability

3.2.1.1.1 Principle - Mercury is desorbed from impregnated charcoal collectors and analyzed directly for mercury with an atomic absorption sampling boat assembly in an oxidizing air-acetylene flame. Measurements are made based on the absorption of the mercury resonance line at 2537 Å.

3.2.1.1.2 Applicability - Technique was devised to measure mercury vapor, volatile mercury compounds, and mercury-bearing dust in industrial samples. Dusts were retained on glass wool, and the volatile mercury and its compounds were adsorbed on the impregnated charcoal. Although a manual technique, the total analysis time for one air sample is less than three minutes.

Speed, sensitivity, collection efficiency and apparent freedom from interferences are major advantages. Main disadvantages are manual operation and open flame excitation.

3.2.1.2 Range and Sensitivity

Limit of Detection - 0.02 μg Hg for a 10-liter (0.01 m^3) air sample.

3.2.1.3 Interferences

3.2.1.3.1 Chemical - All commercially available impregnated charcoal for mercury must be heated at 600-800°C for one hour prior to use. The procedure removes excess impregnant and all interfering volatile organic solvents from the charcoal.

Author found that levels much greater than threshold "limit values" of benzene, toluene, acetone and carbon tetrachloride which absorb 2537 Å radiation must be present, before sufficient amounts are adsorbed on the charcoal to interfere with the analysis of atmospheric mercury.

3.2.1.3.2 Physical - Tantalum boat deteriorates after repeated use and a standard sample must be analyzed after every 4 or 5 samples to determine loss in sensitivity. Boat must be replaced when analytical sensitivity falls to about 75% of the initial value.

3.2.1.4 Accuracy, Precision and Stability

No specific data are given; authors imply that method is more precise than other ultraviolet methods at levels less than 0.02 mg/m^3. Trapping efficiencies appear to be excellent with no apparent slippage to second unit of charcoal.

3.2.1.5 Apparatus

3.2.1.5.1 Atomic Absorption Spectrophotometer - Perkin-Elmer Model 303 or equivalent.

3.2.1.5.2 Tantalum Sampling Boat System

3.2.1.5.3 Triple Slot Burner - Oxidizing air-acetylene flame.

3.2.1.5.4 Recorder Read-out - Equipped for total system scale expansion of 5X.

3.2.1.5.5 Impregnated Charcoal - Barnebey-Cheney Co. Type 580-12 or 580-20 (20-40 mesh). (Note - Charcoal impregnated with trace amounts of iodine and iron powder greatly increase adsorption efficiency of activated carbon for mercury, without interfering with recovery of trapped mercury.)

3.2.1.5.6 Sampling Tube - 6-in. long, 4-mm diameter, packed with two one-inch sections (180 mg each) of charcoal. The two charcoal sections are separated and retained by fiberglass plugs.

3.2.1.6 Time Cycle for Sampling and Measuring

Ten liters of air are taken for analysis, but no data on sampling rates are reported. The total analysis time for one air sample is less than three minutes.

3.2.1.7 Calibration Procedure

Calibration curve prepared from atomic absorption standards containing known amounts of mercury.

3.2.1.8 Method of Sampling and Sample Preparation

Mercury vapor and its volatile compounds trapped on impregnated charcoal are desorbed from the charcoal in the air-acetylene flame of an atomic absorption spectrophotometer. The charcoal is introduced into the flame in a tantalum boat (std. PE accessory).

3.2.1.9 Multi-element Application

By varying instrument conditions, flame temperatures, and radiation sources, a variety of individual elements could be determined, but not a large number simultaneously.

3.2.1.10 Physical Dimensions

Laboratory instrument (atomic absorption spectrophotometer) approximately 5' x 2' x 2'.

3.2.1.11 Unit Output

Response convertible to mass (micrograms) or mass/volume.

3.2.1.12 Safety Hazard

Intense, open flame.

3.2.1.13 Recommendations for Method Improvement

As designed, the method involves manual operation and consumable charcoal samplers and is not directly applicable to continuous monitoring. Consideration should be given to the design of a thermal desorption system which would permit cycling of the collection tube. Obviously, a study of the trapping efficiency deterioration during cycling is needed. Loss of iodine may be a major problem. Desorption with induction heating, rather than the air-acetylene flame, should be considered.

3.2.1.14 Reference

Moffitt, A. E. and R. E. Kupel, "A Rapid Method Employing Impregnated Charcoal and Atomic Absorption Spectrophotometry for Impregnated Charcoal and Atomic Absorption Spectrophotometry for the Determination of Mercury in Atmospheric, Biological, and Aquatic Samples," Atomic Absorption Newsletter, 9, 113-118 (1970).

3.3 Emission Spectroscopy

Generally, direct application of spectrographic analysis for mercury is reported as unsatisfactory. However, this observation is based on the analyses performed by excitation of batch samples from crater electrodes. The problem is volatilization of the metal from the crater of the electrode prior to its activation. This problem should not exist when the mercury containing airborne specimen (vapor or particulate) is passed continuously through the excitation zone of an arc, spark, and radiofrequency or microwave induced plasma.

The technique of Webb, et al (ref. 26,27) used for monitoring beryllium in air continuously, or Fromm and V. Oer (ref. 28) used for measuring beryllium and mercury in air should be applicable to monitoring mercury from stationary source emissions.

Excitation of optical emission at 2537 Å with low power microwave radiation (ref. 29) resulted in a detection limit of 0.1 nanograms. (Note - Lower limits are possible.) This approach is presented in more detail in the following sub-section.

3.3.1 Determination of Mercury Compounds by Emission Spectrometry in a Helium Plasma

3.3.1.1 Principle and Applicability

3.3.1.1.1 Principle - Optical emission of the 2537 Å atomic mercury line is induced with a microwave-powered inert gas (helium) plasma generated at a pressure of 5 to 10 mm. The intensity of the emission is related to the quantity of organo-mercury compound present in the effluent from a gas chromatographic system.

3.3.1.1.2 Applicability - Technique was developed as a gas chromatographic detection system to measure extremely low concentrations of organo-mercury compounds which were separated chromatographically and would be isolated in an inert gas matrix. The detector could be applied to the measurement of mercury vapor and volatile mercuric compounds in an inert gas matrix.

Gas chromatographic isolation of the organo-mercury compounds in the inert and monoatomic, helium matrix of the gas chromatographic effluent is necessary to minimize the quenching effect on the microwave excited plasma by molecular species, e.g., H_2O, O_2, N_2, organic solvents, present in the original sample.

The application to the direct analysis of total mercury in air is doubtful unless an inert matrix (helium or argon) can be substituted for the air. This would be possible through a mechanism involving chromatographic removal of the air from an aliquot sample, or (less likely) if the concentration of mercury and instrument sensitivity were high, by dilution with an inert gas.

3.3.1.2 Range and Sensitivity

Range - Linear response from 0.1 to at least 100 nanograms of methylmercuric chloride.

Sensitivity - 0.1 nanogram as dimethylmercury or methylmercuric chloride.

3.3.1.3 Interferences

3.3.1.3.1 Chemical - No interferences when used as a chromatographic detector. There is some question whether excessive molecular species would quench the helium plasma in non-chromatographic applications.

3.3.1.3.2 Physical - Technique is restricted to measurements involving vapor forms of mercury. Direct analysis of mercury particulate is doubtful unless metallic mercury could be generated in a pre-analysis step.

3.3.1.4 Accuracy, Precision and Stability

Data obtained for methylmercuric chloride was comparable to that determined with an electron capture detector.

3.3.1.5 Apparatus

3.3.1.5.1 Discharge Tube - 1.5-mm bore, 8-mm o.d. quartz tube.

3.3.1.5.2 Cavity - Tapered microwave 2450 MHz cavity fitted with two irises to facilitate tuning.

3.3.1.5.3 Ancillary Equipment - Recorder, power supplies, flowmeters and pressure regulators.

3.3.1.6 Time Cycle for Sampling and Measuring

Approximately four minutes of chromatographic time is required to isolate methylmercuric chloride in the helium matrix for measurement with the emission detector. The excitation and recording of the optical emission requires less than one minute.

3.3.1.7 Calibration Procedure

Known amounts of organo-mercury compounds were injected into the gas chromatograph.

3.3.1.8 Method of Sampling and Sample Preparation

Known volumes of liquid sample were injected into a gas chromatograph.

3.3.1.9 Multi-element Application

Could be modified for application to other volatile metal- and nonmetal-containing compounds.

3.3.1.10 Physical Dimensions

No data given, but detection unit should be relatively small.

3.3.1.11 Unit Output

Recorder (mv) readings convertible to mass units (nanograms).

3.3.1.12 Safety Hazard

Moderate electrical voltages.

3.3.1.13 Recommendations for Method Improvement

Consideration should be given to use of a several stage system to (a) thermally decompose mercury compounds and particulate into mercury vapor, (b) separate elemental mercury from the air matrix (chromatographically or collection system), and (c) use the low pressure helium plasma (microwave induced) to measure the total amount of mercury present in air samples. Analytical times less than 5 or 10 minutes are possible.

3.3.1.14 References

Bache, C. A. and D. J. Lisk, "Gas Chromatographic Determination of Organic Mercury Compounds by Emission Spectrometry in a Helium Plasma," Anal. Chem. 43, 960-963 (1971).

Bache, C. A. and D. J. Lisk, "Simple Tuning Device for Microwave Tapered Matching Cavity," Anal. Chem. 40, 2224 (1968).

Bache, C. A. and D. J. Lisk, "Selective Emission Spectrometric Determination of Nanogram Quantities of Organic Bromine, Chlorine, Iodine, Phosphorus, and Sulfur Compounds in a Helium Plasma," Anal. Chem. 39, 786-789 (1967).

3.4 Formation of Colored Complexes

Several methods for measuring atmospheric mercury vapor have been developed based on the reaction of mercury with copper diiodide to form a double Hg-Cu iodide salt ($CuI \cdot HgI_2$). The reaction has been used in several forms: (a) Hg absorbed in I_2 and KI solution (ref. 30,31), (b) CuI_2 deposited on silica gel (ref. 32), and (c) CuI_2 deposited on filter paper (ref. 33,34). Depending on the sampling time (5-20 minutes), detection of mercury vapor in air down to <0.15 µg/l is reported.

The most promising of the approaches for short-term intermittent monitoring would be a modified version of Palalau method (ref. 34). The method is based on the color formed when mercury vapor in the atmosphere reacts with copper diiodide on filter paper. Color varies from cream-white to orange-yellow as a function of the mercury concentration; color intensity is measured by determining the luminosity intensity of the paper at 510 nm with a spectrophotometer adapted to reflectance measurements.

3.5 Neutron Activation Analysis

The lengthy cooling times (20-30 days) required after irradiation and prior to counting preclude the application of neutron activation analysis (NAA) to continuous monitoring of mercury in complex matrices similar to typical ambient air particulate. For nondestructive NAA measurements (no radiochemical separation), a commercial activation analysis service reports a detection limit of 0.810 µg Hg for particulate matter (∿14 mg) collected from urban air. By using radiochemical separations, the activation analysis service coutinely determines mercury to 3 nanograms in a 1-gram sample and to 10 parts per trillion in 50-g samples with extended irradiations (up to 100 hrs).

In other nondestructive neutron activation analyses of air pollution particulates (ref. 35,36), detection limits of 0.01 µg Hg are reported after irradiation for 2-5 hours, cooling for 20-30 days, and counting for 4000 seconds.

3.6 Radioisotopic Method

Magos (ref. 37), and Magos and Clarkson (ref. 38) developed an isotopic method for determining metallic mercury in air. The sample is passed through a solution containing Hg(II) as a complex salt or chelate, e.g., EDTA complex with ^{203}Hg. The ^{203}Hg released from the reagent into the gas stream is absorbed in Hopcalite or $KMnO_4$ and measured with a scintillation counter. Good reproducibility is reported for 0.016 to 1.2 µg Hg/liter of air.

3.6.1 Radiochemical Determination of Mercury Vapor in Air

3.6.1.1 Principle and Applicability

3.6.1.1.1 Principle - Air containing mercury is passed through an aqueous solution of ^{203}Hg-mercuric acetate and KCl to promote isotope exchange. The issuing air contains the same concentration of mercury, but labelled and with the same specific activity as the reagent solution. The ^{203}Hg is absorbed on Hopcalite and estimated by gamma scintillation counting.

3.6.1.1.2 Applicability - Method can be used for short term sampling (5 minutes) or continuous monitoring of metallic mercury vapor in air at flow rates of 0.5 to 1.5 liters/minute.

3.6.1.2 Range and Sensitivity

3.6.1.2.1 Range - Range is approximately 0.01 μg/liter to 1.2 μg/liter.

3.6.1.2.2 Sensitivity - Detection limit depends on the amount of sample collected, but is approximately 0.01 μg/liter.

3.6.1.3 Interferences

3.6.1.3.1 Chemical - No effects were observed with test mixtures of 1% household gas (containing 10% carbon monoxide), 1% acetylene, 2% CO_2 and 0.1% SO_2.

Effect of H_2S was only determined qualitatively. H_2S produced a black precipitate in the reagent and a rapid decrease in the efficiency of the exchange reaction. This effect was prevented by using a midget impinger with 15 ml 2% cadmium chloride solution or 1N NaOH before the reagent.

The lack of interference from SO_2 bears noting since solutions containing chloride/$HgCl_2$ in the ratio of 2:1 can form stable disulphitomercurate complexes (see West and Gaeke method for absorbing SO_2). Fortunately, with higher ratios, as used in the exchange reagent, the stability of the complex decreases - if it is formed at all.

High concentrations of air contaminants, which react with Hopcalite (solid mixture or copper and manganese oxide), can exhaust the absorber in prolonged tests.

The efficiency of the exchange reaction was not affected by pH changes from a normal of 6.2 to 9.6 with NaOH addition or to 1.5 with citric acid added.

3.6.1.3.2 Physical - Temperature of the reagent bath had no influence on the exchange reaction in the range 5°C to 30°C, but at 9°C, the efficiency decreased by approximately 14%.

Variations in air-flow from 1.0 liter/minute to 1.5 liter/minute produced no effect. However, reduction in flow to 0.5 liter/minute resulted in increased efficiency of approximately 3.5%.

3.6.1.4 Accuracy, Precision and Stability

The standard deviation of the method is 0.004 μg/liter in concentrations up to 0.2 μg/liter, and is 0.075 μg/liter in the range 0.2-1.2 μg/liter.

3.6.1.5 Apparatus

3.6.1.5.1 Collection Train - Flow regulator and flowmeter; 30 ml impinger containing 20 ml reagent; one or more Hopcalite absorbers.

3.6.1.5.2 Exchange Reagent - 2.5 x 10^{-4}M mercuric acetate and 0.25M potassium chloride in glass distilled water labelled with $^{203}Hg^{++}$. (Note - Increase in mercury concentration caused by labelling was always less than 1.0%.) Reagent usually contained <2 μc/20 ml.

3.6.1.5.3 Radiochemical Detector - Well-shaped NaI (gamma) scintillation detector (Detector N664B) with a scaler (N610A, Ekco Electronics, Ltd) having a counting efficiency for ^{203}Hg of 40%.

3.6.1.5.4 Absorbers - Polyallomer tubes (5/8 x 3-in.) (Beckman Instr. Inc., Spinco Division) containing 3 g of activated Hopcalite (solid mixture of copper and manganese oxide). Inlet and outlet tubes were Sterivac polythene cannulae (bore 2.0 mm, wall thickness 0.5 mm).

3.6.1.5.5 Ancillary Equipment - Lead shielding for midget impinger, suction pump, special saturation system for calibration, recorder.

3.6.1.6 Time Cycle for Sampling and Measuring

Measurements can be made continuously if the absorber is kept in the well of the gamma scintillation counter. Short-term sampling can be accomplished in 5-minute sampling cycles followed by removal and replacement of the absorber tube. Counting times are usually 100 seconds.

Sampling times are dependent on the analysts requirements for precision and sensitivity and can range from 2-20 minutes.

3.6.1.7 Calibration Procedure

Calibration was based principally on literature data for the concentrations of mercury vapor in air at saturation at various temperatures. Air was saturated with mercury at various temperatures and introduced directly or after dilution with known amounts of additional air.

A specially designed 1 μg calibrator was fabricated from a plastic syringe. The syringe provided a way to deliver a volume of mercury saturated air containing 1 μg mercury without the errors which may attend mixing two air streams.

Calibration of the technique with the 1 μg calibrator also provided a means for measuring the efficiency of the exchange reaction (97.7%) to incorporate a correction factor for the absorbed (Hopcalite) activity.

Since the efficiency of one absorber was considered quantitative (99.4%) and within counting errors, no correction for absorption efficiency was required.

3.6.1.8 Method of Sampling and Sample Preparation

Air samples containing metallic mercury vapor are drawn through an isotope exchange solution at 1 liter/minute. Radioactive Hg produced in the isotope exchange is absorbed on Hopcalite and counted with a gamma scintillation counter.

3.6.1.9 Multi-element Application

Methodology is specific for mercury; however, by suitable changes in reagents and absorber, applications to other volatile elements having radioactive isotopes are possible.

3.6.1.10 Physical Dimensions

No data reported; collection train and absorption system would be relatively small. A laboratory-type scintillation counting system was used and undoubtedly would be the largest component.

3.6.1.11. Unit Output

Counts/100 seconds convertible to μg Hg or μg Hg/liter.

3.6.1.12 Safety Hazard

Moderate electrical voltages are used in conventional amplifiers, etc. Radioactivity could be minor problem, but low activity in the reagent (<2 μc/20 ml) and Hopcalite permits disposal as normal waste.

3.6.1.13 Recommendation for Method Improvement

Application of improved gamma radiation measurements with semi-conductor detectors may permit shorter sampling and counting times, and higher sensitivities.

3.6.1.14 References

Magos, L., "Radiochemical Determination of Metallic Mercury Vapour in Air," Brit. J. industr. Med. 23, 230-236 (1966).

Magos, L. and T. W. Clarkson, "Isotope Method for Determining [Metallic] Mercury in the Air," Brit. 1,130,921 (16 Oct. 1968); C.A. 70, 14229p.

3.7 Argon Ionization Detection

Krestovnikov and Sheinfinkel (ref. 39) collected mercury on activated carbon and desorbed the mercury into a stream of argon to be detected with an argon ionization detector (three electrode type with 10 mg ^{147}Pm radioactive source). Results agreed well with those of a colorimetric method and indicated a detection threshold of 1 x 10^{-5}g/l with collection time of 10 minutes.

By improved detector and electronic design and by using gold wool as a trapping system, greater sensitivity and collection efficiency can be attained which would permit shorter term cycles for intermittent (<10 minute) monitoring of stack emissions.

3.8 Condensation Nuclei Monitor

Environment One Corporation manufactures a Mercury Vapor Detecting System consisting of two units, a Mercury Converter and a Condensation Nuclei Monitor, for measuring total atmospheric mercury. Mercury, collected by drawing air through a cartridge containing a plug of silver wire is desorbed with heat into a cloud chamber. The desorbed mercury vapor is irradiated by ultraviolet light, forming submicroscopic particles of HgO. Water vapor condenses on the nuclei in the cloud chamber and droplets are formed which may be counted by optical and electronic circuits.

Preliminary tests at Battelle's Columbus Laboratories indicate insufficient sensitivity, unsatisfactory duplication of replicate samples and questionable short term stability (ref. 40).

4. SAMPLE COLLECTION TECHNIQUES

In most cases of ambient air monitoring, some collection or pretreatment procedure is used to concentrate the mercury or to eliminate interfering materials. A variety of sample pretreatment or collection steps are used and representative types are listed in Table II. Generally, the mercury is collected as vapor in impingers containing various fluids, on activated or modified carbon, or on a variety of metals which form amalgams.

As shown in Table II, many collection techniques can be used for specific forms of mercury, but there is no universal collecting media for all forms. Two media - 0.1N iodine monochloride in 0.5M hydrochloric acid (I), and fluidized bed of activated carbon impregnated with iodine (II) - have been applied to a greater variety of mercury forms than the others. However, the efficiency of (I) for collecting airborne mercury particulate has not been fully tested. By arranging a special sequence of collecting media, complete collection of all forms of mercury emissions are possible. A particulate filter combined with either (I) or (II) would provide a good, general collection system.

Table II

COLLECTING MEDIA FOR MERCURY AND ITS COMPOUNDS

Collecting Media	Mercury Form	Efficiency	Ref.
Water	Mercury-bearing dusts	Adequate	41
25% Ethanol in water	Mercury-bearing dusts w/fat and oil	Adequate	41
Aqueous solution sodium carbonate	(a) Mercury vapor (b) Monomethyl and ethyl mercury salts	Not retained Quantitative	42
1N Hydrochloric acid	Mercury vapor	Adequate	43
Alkaline hyprobromite	Mercury vapor	90% (1st stage) 99-100% (2nd stage)	44
Aqueous solution NaOCl[1]	Mercury vapor	>99%	44
Aqua regia-water (1:3) spray	Mercury vapor	<5%	45
Acid permanganate solution (several conc.)	(a) Mercury vapor	Adequate	46 & 47
	(b) Alkylmercurials (c) Monomethyl & ethyl mercuric salts	Poor	68
0.1N Permanganate	(a) Mercury vapor (b) Dibutylmercury	Adequate Poor	48
0.5N Potassium permanganate in 2N sulfuric acid	Dimethylmercury	<5%	40
Aqueous iodine (0.25%) and potassium iodide (3%)	(a) Mercury vapor (b) Mercury bearing dust	Adequate	41 & 50
	(c) Dimethylmercury (d) Diethylmercury	<20%	
Aqueous iodine (0.12%) in 1.5% solution of KI	(a) Mercury vapor	Quantitative	51
	(b) Diethylmercury (c) Ethyl mercuric chloride	Negligible at 20 liters/minute	
Isopropanol	Dibutylmercury	Adequate	48

Table II - (Cont'd)

Collecting Media	Mercury Form	Efficiency	Ref.
Alcoholic iodine (0.08%)	(a) Mercury vapor	Quantitative at 25 liters/minute	51
	(b) Diethylmercury		
	(c) Ethylmercuric chloride		
Cold trap	Mercury vapor	Adequate at flow rate <5 liters/minute	52 & 53
0.1N Iodine monochloride in 0.5M hydrochloric acid	(a) mercury vapor	95-100%	49
	(b) Dimethylmercury	90-100%	
	(c) Diethylmercury		
	(d) Ethylmercury chloride[2]	90-100%	
	(e) Methylmercury chloride[2]	100%	
	(f) Phenylmercury chloride[3]	100%	
	(g) Mercury oxide[3]	88 to 92%	
	(h) N-(Ethyl mercury) p-toluene sulfonamide[3]	94%	
Solid crystal iodine	(a) Mercury vapor	Adequate	49
	(b) Diethylmercury	<20%	
Activated carbon	Mercury vapor	Adequate	54
Activated carbon w/Cl	Diethylmercury	Adequate	55
Fluidized bed of activated carbon	(a) Mercury vapor[4]	<4%	56
	(b) Diethylmercury	90-100%	
	(c) Diphenylmercury		
	(d) Ethylmercury chloride		
	(e) Ethylmercury phosphate		
	(f) Methylmercury dicyandiamide		

Table II - (Cont'd)

Collecting Media	Mercury Form	Efficiency	Ref.
Cadmium sulfide-glass fiber	(a) same as fluidized bed of carbon with exception of diethylmercury (b) Mercury-bearing dust	 Adequate	56
Activated MnO_2	Mercury vapor	Adequate	57
$MgSO_4$, KI, I_2, H_2O, glycol, acetone[5]	Mercury vapor	Quantitative	58
Filter paper impregnated w/aqueous solution 4.6% I_2 and 55% KI	Mercury vapor	>92%[6]	
Palladium chloride	Mercury vapor	Quantitative	60
Selenium sulfide coated filter paper at 65°C	Mercury vapor	Adequate	61
Selenium impregnated filter paper	Mercury vapor	Adequate	62
Silver foil amalgamator	Mercury vapor	Good	63
Silver sponge[7]	Mercury vapor	Good	64 & 65
Gold leaf	Mercury vapor	<5%	45
Gold wire (∿14 cm^2) @ 600°C	Mercury vapor	95%	66
Gold impregnated glass frit or asbestos	Mercury vapor	Quantitative at 2 ft^3/hr	67
Gold foil	Mercury vapor	Quantitative	69
Gold wool (25°-250°C)	Mercury vapor	Quantitative	70,71,72
Copper spiral	Mercury vapor	Quantitative	73
Copper diiodide	Mercury vapor	Quantitative	34
Copper foil	Mercury vapor	Quantitative	74

Footnotes - (Table II)

[1] 1 g available Cl/liter and 100 g NaCl/liter at pH 10.7 and 50°C.

[2] Trapped as vapor or added as solid directly to ICl reagent.

[3] Added as solid directly to ICl reagent.

[4] Fluidized bed of iodized carbon would be satisfactory for mercury vapor.

[5] 14 g anhydrous $MgSO_4$, 1.2 g KI, 0.1 g I_2, 0.4 ml H_2O, 1 ml ethylene glycol and 12 ml acetone.

[6] Requires humidifier prior to filter to attain high efficiency.

[7] A pre-filter @ 800-900°C of decomposed $KMnO_4$ (prepared @ 600°C) is used to remove N oxides, halogens, S-, P-, Sb-, Se, -, As-containing compounds.

5. SAMPLE PRETREATMENT

As an alternative to a sequence of collecting media to isolate mercury particulate, elemental mercury vapor, and organic or inorganic bound mercury, thermal decomposition techniques which convert the total mercury to one form, elemental mercury, can be used. Decomposition of bound mercury to elemental mercury vapor produces a form of mercury which can be easily collected or measured directly.

The major problems in performing quantitative thermal decompositions of mercury compounds are the variations in compound stability. Unless the heating is performed rapidly at high temperature or a moderately long residence time is used, volatile halides and organomercurials may not decompose but escape as undercomposed vapor. Very hot oxyhydrogen flames, combustion in air in furnaces at 800-900°C, and thermal decomposition in presence of reducing media (iron powder and CO, or $SnCl_2$) have all been used. Representative techniques are reported in the following summaries.

5.1 Thermal Decomposition with Fe and CO

Mercury dust is sublimed at 700°C for 30 minutes in a specially designed quartz tube. Iron powder is used as a reducing agent, and CO is used as a carrier gas to expel mercury vapor. An asbestos filter is used to retain sulfur and other components interfering with the mercury determination. Mercury vapor in the CO stream is absorbed by a 0.2% solution of I_2 in 2% KI and determined colorimetrically with a sensitivity down to 0.2 ppm of Hg in the dust (ref. 75).

5.2 Thermal Decomposition in Air, Nitrogen or Oxygen

Sample powder containing organic or inorganic bound mercury is burned in a 35-cm silica tube of 12-mm inner diameter in a stream of N_2, O_2, or air at 15-20 ml/min. at 800-900°C. The evolved Hg is absorbed on Ag sponge in a 3.5-cm silica tube of 8-mm diameter. Volatile elements (P, As, Sb, S, Se, Te, F, Cl, Br, and I) are removed by a 12-cm section of $KMnO_4$ decomposition product (prepared at 600°C) placed in the combustion tube. The errors in determining 1%, 0.1%, 0.01%, and 0.001% were ±0.1%, ±0.01%, ±0.001%, and ±0.0002%, respectively (ref. 65).

5.3 Thermal Decomposition at 1200°C

Mineral sample (85 mesh) is heated up to 1200°C for 1 to 95 hours in a closed system to release mercury vapor (ref. 52).

5.4 Combustion at 850°C in Air

Combustion of 25 to 50 mg samples of mercury-containing materials is attained in an air stream (100 cc/min) in less than five minutes with gas burner or electric coil heating in a heating cycle from room temperature to 850°C (ref. 67).

5.5 Decomposition of Powdered Samples at 850°C

Powdered samples containing 0.001-1% Hg (from the Sn industry) were heated at 750-850°C in a stream of air (5-7 liters/minute) for approximately 2-3 minutes, yielding photometric analyses with coefficient of variation of 3-4% (ref. 76).

5.6 Reaction with $SnCl_2$ and Thermal Vaporization

Powdered sample is mixed with $SnCl_2$ to reduce mercury compounds; electrical heating of system vaporizes the mercury for measurement with atomic absorption techniques. Sensitivities reach 10^{-6}% Hg in powdered solid material with an average relative error of 10-15% (ref. 77).

5.7 Reaction with Na_2CO_3-K_2CO_3-Na_2O_2

Organic or inorganic sample is heated at 650°C with 12:1.6:4 Na_2CO_3-K_2CO_3-Na_2O_2 in an air stream to distill elemental mercury (ref. 78).

5.8 Thermal Decomposition of Powdered Geological Samples

Pulverized ores and geological samples (up to 150 mesh) were heated in a tube furnace under forced gas flow. Evolved mercury vapor was measured by atomic absorption spectrophotometry yielding analyses down to 3×10^{-8}% at sample weight of 0.5-2 g in approximately 3 minutes. The error of a single determination varied from 8 to 30% (ref. 79).

5.9 Thermal Decomposition - Addition of Lime

Decomposition of sulfide-containing dusts, soils and minerals is accomplished with gas-fired flame in the presence of lime at a sample to lime ratio of 1:2. Small quantities of interfering sulfides are eliminated by reaction with the lime. For 0.25 g sample, approximately 10 minutes are required (ref. 80).

5.10 Thermal Decomposition of Organo and Metallic Mercury Compounds at 800°C

Total mercury in atmospheric dusts and vapors was determined by mercury vapor photometric readings after thermal decomposition of organo-mercury and inorganic mercury compounds in a continuous flow system. Furnace temperature was 800°C and the air flow was set at 5 liters/minute (ref. 81).

5.11 Thermal Decomposition and Removal of Sulfur Compounds with Na_2CO_3

Inorganic pigment samples were heated directly and the amount of mercury liberated was determined by the photometric mercury vapor procedure. Interference due to presence of S was avoided by igniting the sample while mixed with Na_2CO_3 and and passing the evolved gases through a silica gel trap (ref. 82).

5.12 Decomposition in Oxyhydrogen Flame

Mercury containing organic and inorganic compounds were decomposed in a hot oxyhydrogen flame of burner assembly of a flame photometer. The exhaust gases pass through condensers and filter towers and then finally through the cell of a mercury vapor meter for measurement (ref. 11).

5.13 Pyrolysis at 650°C and Removal of Interfering Substances with a Series of Traps

Organic and inorganic samples are pyrolyzed at 650°C, generating mercury vapor from the mercury compounds present in the sample. The pyrolysate is passed over heated copper oxide and swept through a series of traps (silver vanadate, Ascarite, Dehydrite, and anhydrous alumina) to remove interfering substances. The mercury content of the gas stream is determined with a commercially available mercury vapor meter. Amounts of mercury as low as 0.01 μg can be detected (ref. 83).

5.14 Pyrolysis at 700°C and Removal of Interfering Substances with Silver Reaction Chamber Followed by Gold Amalgamation

Thermal decomposition is used to convert chemically bound mercury into mercury vapor. Silver wire removes chlorides and gold foil isolates the mercury from the remaining contaminants. Mercury desorbed by heating the gold amalgam is measured with an atomic absorption spectrophotometer (ref. 84).

6. TECHNIQUES FOR GENERATING KNOWN CONCENTRATIONS OF MERCURY VAPOR IN AIR

Current methods for producing known concentrations of mercury have several deficiencies: (1) air and mercury are usually not sufficiently heated to produce a saturated gas stream on cooling, (2) excessive time is required to reach equilibrium after concentration changes have been made, and (3) large size of condensation and mixing vessels and the need for bulky constant temperature apparatus limit field use.

The mercury vapor generator developed by Nelson, et al. (ref. 85) and Nelson (ref. 86) occupies 0.1 m^2 of bench space and yields concentrations from 0.011 to 2.5 mg/m^3 at flow rates of 6 liters/minute or greater with an accuracy of ±3%. Concentration changes are made simply and equilibrium is reached almost instantaneously.

Chase, et al. (ref 40) constructed an apparatus employing a permeation tube to supply a constant amount of mercury vapor in a gas stream. The permeation tube contained 10 grams of mercury in a 7/8-inch section of silicone rubber tubing (1/2-in. ID, 3/16-in. wall thickness) and was plugged on both ends with teflon. By maintaining the permeation tube at 31°C and by passing nitrogen gas maintained at 31°C over the tube at 220 ml/min., a mercury vapor flow of 15 ± 1 ng/min. was attained after an equilibration period of 24 hours.

Considerable differences exist in data reported for mercury vapor pressure over the 20° to 30°C temperature range. Nelson, et al. (ref. 85), Mayer (ref. 87), and Ernsberger and Pitman (ref. 88) indicate similar data, but differ markedly with data by Hill (ref. 89,90).

7. PROBLEMS COMMONLY ENCOUNTERED IN MERCURY ANALYSIS

Most direct analyzers (photometers) and collection systems for air atmospheres measure or collect elemental mercury vapor only. Although filter devices can collect particulate and a variety of impinger fluids have been used for organomercurials, no single, efficient collection system for total mercury is available. Most promising solution to the problem is conversion of all forms of mercury to elemental vapor by thermal decomposition.

Particulate (smoke, dust, etc.), iodine, sulfur compounds, organic compounds, and ozone, interfere with the highly sensitive, inexpensive mercury vapor photometric method of analysis. Several instrumental solutions to the problem are possible by compensating for the background signal. Alternate means of trapping the mercury as an amalgam with subsequent desorption as elemental mercury vapor provide an efficient solution.

Sulfides, naturally present in a sample stream or as decomposition products of sulfates and sulfur compounds in a flame, may remove elemental mercury vapor. A solution to the problem uses gold to amalgamate the mercury prior to any filter on which the sulfide can be deposited. After venting the contaminating gases, the mercury is desorbed for analysis.

Iodides trapped in filters may also combine with mercury in similar manner as sulfides. Use of a collection step with gold will also minimize the potential loss.

Mercury losses occur during processes using sample collection because of adsorption effects, hydrolysis, and decomposition into metallic mercury which evaporates. The presence of adsorbed moisture on glass surfaces can cause removal of elemental mercury from air or gas streams. Lindstrom (ref. 11) reports that borosilicate glassware which had been cleaned with sulfuric acid-dichromate solution shows negligible adsorption. However, silicone-treated glassware cannot be used because of adsorption effects (ref. 11). (Note - Lindstrom's observations differ somewhat with regard to observations with other metals and undoubtedly depend on many additional factors, e.g., form of compound, i.e., organo-mercurial, inorganic salt, etc., and must be evaluated independently depending on the application.)

Cellulose filter paper strongly adsorbs mercury.

Studies using centrifugation of solutions show that mercury from clear solutions can be removed by adsorption on invisible dust particles.

Decomposition of many mercury derivatives to metallic mercury can result in rapid loss of the more volatile elemental mercury. With dilute solutions of mercury compounds, particularly at a neutral pH, the loss due to decomposition into metallic mercury, which has a low solubility and high vapor pressure, can be extensive.

In systems which use a collecting medium followed by reduction of Hg by $SnCl_2$ directly in the atomizer of an absorption flame photometer, several chemical interferences are observed. CN^-, I^-, $S_2O_3^=$ interfere and over 1 mg As(III) or $\geq$0.1-0.2 mg Se(IV), Te(IV), Cr(VI) and Mn(VII) per cubic centimeters interfere.

Relatively high concentrations (100 μg/ml) of cobalt produce a 10% spectral absorption interference in the atomic absorption determination of mercury. The Co line at 2536.49 Å, which causes the interference when determining Hg at 2536.52 Å in a Co matrix, arises from a metastable state.

The application of gold wool or foil to separate mercury from interfering components is an excellent approach. Although only slight deterioration of efficiency has been observed with continued use, some consideration should be given to a potential problem with gold amalgams which have picked up marked quantities of lead and tin. When such amalgams are heated, mercury does not evaporate. The amalgams explode into small pieces.

Unless extensive shielding is used, the mercury vapor photometers cannot be used in the vicinity of high magnetic fields (electrolytic preparation of chlorine and caustic soda).

Several problems can be encountered in attempting to collect mercury salts. Absorption in liquids can be incomplete since particles between 5μ and 25μ may pass through. Use of a filter coupled with an absorption device is recommended. The absorption device should be used to back the particle filter to minimize the volatilization of the mercury salts due to the continuous passage of air through the filter and over the mercury compounds, e.g. halides, which have relatively high vapor pressure.

Hwang, et al. (ref. 91) thoroughly investigated analytical variables of the technique using chemical reduction ($SnCl_2$) of air-borne mercury and its compound collected in $KI-I_2$ reagent and flameless atomic absorption measurements. They concluded (a) that argon, rather than air, should be used as a purge gas to minimize oxidation of Hg; (b) low results occur when using $SnCl_2$ as a reducing agent with $KI-I_2$ collecting media (hydrazine hydrate should be used); (c) non-specific background absorbance due to light scattering from aerosol droplets, etc., can be minimized with a reference deuterium lamp, automatic background correction; and (d) care, regarding working curve range, mixing time, sample volume, and flow rate of flushing gas, must be taken.

Nelson (ref. 86) encountered considerable response irregularities when using grille-type instruments, as opposed to self-sampling orifice-type mercury vapor detectors (photometers). With the high sensitivity scale (0 to 0.1 mg/m^3), and if the photometers were zeroed on still air, any pure air flow through the grill-type photometer caused a positive needle deflection. The grill-type photometer must be zeroed with a flow rate of pure air just equal to the flow rate of the mercury vapor-air mixture being tested. The zeroing process must be carried out immediately before the calibration point is to be observed. If this procedure is used, grill-type, photometric, mercury detectors are extremely accurate.

No special zeroing procedure is needed with self-sampling orifice-type instruments (ref. 86).

Nelson (ref. 86) observed that deviations from linearity occurred with grill-type instruments, but not with the self-sampling orifice-type instruments, above 1.0 mg/m^3. When the grill-type detectors were used with mercury in air concentrations in excess of 1.0 mg/m^3, the indicator needle would swing up to a reading of 1.0 mg/m^3 (on a 0-3.0 mg/m^3 scale) and then decrease to a lower value. As the mercury in air concentration became higher, the reading observed became lower.

8. SUMMARY AND RECOMMENDATIONS

At this time, there is no continuous monitoring system which measures total mercury (vapor and particulate) directly. Most monitors are based on the measurements of mercury vapor alone.

The techniques which have sufficient specificity and sensitivity are:

(a) mercury vapor photometry (non-flame atomic absorption)

(b) microwave induced emission spectroscopy

(c) radio-frequency induced or arc excited emission spectroscopy

Mercury vapor photometry measures elemental mercury vapor only and would require a pretreatment step to generate elemental mercury from chemically bound mercury. Also, the technique is subject to interferences from organic compounds, smoke, dust, etc. As a consequence, a compensation technique or removal (physical or chemical) of the interfering materials must be made.

When using low wattage microwave induced emission spectroscopy, a pretreatment step to vaporize particulate or to reduce chemically bound mercury to elemental mercury vapor must be used. The microwave energy (low power) is not sufficient to vaporize particulate directly.

With radio-frequency induced or arc excited emission spectroscopy, sufficient energy is generally available to vaporize particulate up to particle sizes of approximately 80μ at flow rates of 40 liters/minute.

Preheating of the chemically bound mercury to generate and vaporize elemental mercury can be accomplished by induction or resistance heating, oxy-hydrogen or oxy-acetylene flame, ac-dc arc, or rf-plasma.

For each of the techniques measuring emission spectra, sufficient spectral resolution with a monochromator must be available to provide separation of spectral interferences which may arise from the matrix. The mercury vapor photometer system does not necessarily use a monochromator, since the basis of the technique (atomic absorption phenomenon) provides specificity for mercury.

The need for a monochromator in the emission spectroscopy techniques, particularly the low power microwave induced optical emission, can be eliminated if collection-desorption as a gold or silver amalgam is used to isolate the mercury from interfering components of the matrix.

Detection of mercury vapor with an argon ionization system can be accomplished on a short-term, intermittent basis if the bound mercury is decomposed to mercury vapor and the mercury vapor is removed from the matrix with silver or gold amalgamation. Desorption of elemental mercury vapor into the argon ionization detector would produce a highly responsive signal.

Five systems can be identified for potential use as continuous monitors for total mercury in stationary source emissions.

System A

Sample → Thermal decomposition → Compensated mercury vapor photometer

System B

Sample → Thermal decomposition → Isolation as gold amalgams → Mercury vapor photometer

System C

Sample → Thermal decomposition → Isolation as gold amalgam → Microwave induced emission spectroscopy

System D

Sample → Radio-frequency induced or arc excited emission spectroscopy

System E

Sample → Thermal decomposition → Isolation on carbon or as gold amalgam → Argon ionization detection

Although System D does not require a separate thermal decomposition sub-system, it does require a relatively good monochromator to provide spectral resolution. However, with the monochromator, System D provides for multi-element monitoring.

Systems A, B, and C are more sensitive than System D, but require high efficiencies in the thermal decomposition and isolation steps (when needed as in B and C). No information is available on decomposition efficiencies of refractory particulate matrices or at modest to high flow rates. Also, little information is reported on amalgamation and desorption efficiencies of mercury on gold at modest to high flow rates.

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APPENDIX IV

BRIEFING DOCUMENT - ANALYTICAL TECHNIQUES FOR LEAD

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ANALYTICAL TECHNOLOGY FOR CONTINUOUS MONITORING OF STATIONARY SOURCE EMISSIONS FOR LEAD

1. INTRODUCTION

Lead can be present in stack emissions in a variety of chemical forms and may be emitted as fume, dust or organic vapors. The most stable compound and the largest tonnage material used commercially is lead monoxide (PbO).

Lead is well known to be a cumulative poison, with a rated maximum allowable concentration for the industrial 8-hour working day of 150 micrograms per cubic meter. The most toxic compounds are the lead alkyls.

No monitoring system is available at this time for measuring total lead emissions from industrial stacks. Techniques have been developed for measuring the volatile organo-lead compounds in ambient air or inorganic particulate separately, but not continuously and together. Continuous monitoring of stationary source emissions for lead must be able to detect lead as vapor and particulate, and as inorganic or organic compounds.

2. SOURCES AND TYPES OF LEAD EMISSION

Lead enters the environment through natural and man-made processes (ref. 1). It is used to the extent of approximately one million tons per year in almost every type of industry and may escape to the atmosphere as fume, dust, or organic vapors. Industrial emissions may occur during processing of lead containing raw materials, e.g., storage battery manufacture, nonferrous foundries, and production of pigments, coatings, etc. Organo-lead compounds may enter the atmosphere during manufacture of insecticides and gasoline additives. Particulate and fume can be generated in preparing castings, plating for sheet iron, flexible tubes, cable sheathing and lead-lined fittings.

Lead monoxide is commercially the most important lead compound and is prepared by many different processes as a high tonnage heavy chemical. Lead monoxide, principally as αPbO, litharge, is used in preparing storage-battery plates, in compounding in rubber, as an activator in synthesizing sodium plumbite for sulfur removal from gasoline, in formulating glasses, glazes, and enamels, and in making many large tonnage lead compounds. The more important of the latter are basic lead carbonate, basic lead sulfate, basic lead silicate, lead chromate, lead arsenate, red lead, lead soaps, and greases.

Elemental lead has a boiling point of 1740 ± 10°C and a vapor pressure of 1.0 mm Hg at 987°C. Lead monoxide melts at 888°C and has a vapor pressure of 1.79×10^{-3} mm at 670°C. Higher oxides decompose by losing oxygen - Pb_3O_4 (500°C), Pb_2O_3 (370°C), and PbO_2 (290°C).

Lead chlorides, bromides and iodides have boiling points between 900-954°C. The sulfate and sulfite of lead are thermally unstable; lead sulfate begins to decompose when heated in air at about 500°C to yield a mixture of lead oxide and sulfate ($PbO \cdot PbSO_4$) which subsequently decomposes between 900°C and 1000°C to yield lead oxide and sulfur oxides. Lead sulfide melts at 1114°C and lead carbonate decomposes to lead oxide at 315°C.

Organo-lead compounds are relatively volatile - tetraethyllead boils at approximately 195°C with decomposition or at 91°C at 19 mm, tetramethyllead has a boiling point of 110°C, and tetraisopropyllead boils at 120°C at 14 mm.

3. CANDIDATE ANALYTICAL TECHNIQUES

Methods currently used to monitor lead levels in ambient air are based on the principle of isolating the lead compounds by processing large volumes of air. The separation of the lead compounds from air is accomplished either by physical means (filters) to remove particulate or by chemical reaction techniques, in which lead fume, vapor or particulate react with a chemical media to form a stable, relatively non-volatile compound.

Various types of filters - paper, fiber glass, millipore, membrane and microsorban - have been used.

Iodine monochloride is the most efficient of the chemical agents for trapping lead. However, a variety of other materials, including iodine in methanol, iodine in aqueous potassium iodide, iodine in carbon tetrachloride, iodine crystals and dilute nitric acid, have been tried.

The analytical techniques most commonly employed for measuring lead content on the filters or in the chemical trapping solutions include colorimetry (dithizone reaction), atomic absorption spectrophotometry, emission spectroscopy, polarography, and x-ray emission (fluorescence) spectroscopy.

Hundreds of samples of atmospheric airborne particulate containing lead have been analyzed after collecting specimens on filters followed by suitable digestion procedures. Measurements were made with colorimetric techniques (dithizone) (ref. 2), atomic absorption spectroscopy (ref. 3,4,5), mass spectroscopy (ref. 6), x-ray spectrometry (ref. 7), and emission spectroscopy (ref. 8).

Although the sensitivities of these methods are good, the inordinate amount of time used in collecting and preparing the samples precludes the direct application of methodology established in these procedures to monitoring stationary source emissions. Some of the techniques can be modified for use in continuous (or short-term intermittent) analyses of lead from stationary source emissions.

A number of the analytical methods have been applied to measuring volatile organo-lead compounds (alkylleads), but not particulate. Others have been used to determine lead in particulate, but not in vapor. No analytical technique is currently available that can be immediately and directly applied to the analysis of total lead, as vapor, fume, and particulate.

The following sections contain technology related to analytical methods that can be applied to the continuous or short term measurement of lead from stack emissions. Although a variety of techniques are presented, the most attractive methods for general application (vapor and particulate) based on selectivity and sensitivity, are absorption and emission spectroscopy. Others, e.g., x-ray fluorescence, may find application in measuring particulate and some, e.g., gas chromatography, would provide specific analyses for alkyllead compounds.

3.1 Emission Spectroscopy

Aughey (ref. 9) and Koppius (ref. 10) used an emission spectrographic method to monitor lead (particulate and vapor) continuously in air in the range 0.003 mg/ft^3 to 0.05 mg/ft^3. The technique is reported in greater detail in the following subsection and with modification can be adapted to measuring lead emissions from stationary sources.

Additional data relating to emission spectrographic analyses for lead, collected on filters or in liquids are also included to aid in understanding potential interferences and problems that can be encountered.

Although little information is available on the application of electrodeless radio-frequency- or microwave-induced emission spectroscopy to measuring total lead, both techniques can be used. Technology cited in other briefing documents in this series - (a) Beryllium and Cadmium, and (b) Mercury - can also be applied to lead. In applying microwave-induced emission spectroscopy to measuring total lead, a pre-treatment step involving decomposition of particulate (thermal treatment, directly or in a reducing medium) would be necessary.

Razumov and Aidarow (ref. 11) attained absolute sensitivity of 4×10^{-9}g and relative sensitivity of 5×10^{-6}% with spectrographic analyses with an a.c. arc. Measurements were made on the 2833.07 Å lead line for lead in polluted air collected in acetic acid or nitric acid solution. Excitation (40 sec) of an aliquot (0.06 ml) after the addition of a NaCl spectral buffer was accomplished in a carbon electrode which was previously coated with polystyrene. Similar methodology was applied by Yakovleva et al. (ref. 12) in nitric acid solutions of lead collected on an air filter.

Trace quantities (0.15-50 μg) of lead (2823.19 Å) were determined by emission spectrographic analysis of atmospheric dust particles collected on filter paper (ref. 13). The paper was burned in flat graphite electrodes after adding graphite powder. By carrying out the excitation in a magnetic field, the relative standard deviations were decreased from $\leq$15% to $\leq$10%.

Bykhovskaya and Babina (ref. 14) found the emission spectrographic (arc) detection limit of lead to be 0.03 mg in an air sample. The detection in a condensed spark is significantly less sensitive. They also claim that the spectrographic determination of lead shows no advantage over chemical determination either in terms of sensitivity or selectivity, and is disturbed by the presence of tin, copper, and zinc. No data on instrument resolution, nor the emission line wavelength are reported.

Petrova, et al. (ref. 15) report no effect of Fe, Sn, Mn, Cr, Al, Cu, Cd, and Sb on the lead line intensity measured at 2833.06 Å. Some matrix ionization effects are reported for Na and K, but a constant effect can be attained for a wide range of Na and K concentrations.

Improved sensitivity is obtained in the emission spectrographic analysis for lead and other elements by performing the excitation in an atmosphere containing the decomposition products of a fluorinated polymer (Fluoroplast-4). The decomposition products improve the volatility and vaporization rate of the metal element (ref. 16). The obvious extension of this approach is to incorporate low molecular fluorinated hydrocarbons (Freon or perfluorinated alkanes, alkenes, or alkynes) in the continuous flowing stream of lead-containing particulate to aid in the vaporization process in the spectrographic arc or rf plasma. Of course, care must be taken to minimize interaction of the fluorine-containing decomposition products with the materials of construction, e.g., silica.

A continuous method for measuring lead (particulate and vapor), using emission spectrographic analysis, is reported in detail in the following sub-section.

3.1.1 Emission Spectrograph as Mobile Analyzer for Lead in Air

3.1.1.1 Principle and Applicability

3.1.1.1.1 Principle - Air is drawn continuously through a condensed spark discharge where the lead spark emission spectrum is excited. The lead line at 2203.5 Å is measured with a mobile quartz spectrograph equipped with a photographic plate or photoelectric Geiger counter.

3.1.1.1.2 Applicability - Instrument was applied to monitoring lead levels in various manufacturing areas on a semi-continuous basis. The technique measures lead in the form of elemental lead or inorganic or organic compounds of lead. The system is mobile, being mounted on wheels, and has a high degree of specificity and sensitivity.

3.1.1.2 Range and Sensitivity

3.1.1.2.1 Range - Calibration curve shows a range of 0.003 mg Pb/ft^3 to 0.05 mg Pb/ft^3 for a typical operation mode.

Detection limit estimated as <0.003 mg Pb/ft^3 and is determined chiefly by the erratic behavior of the spark discharge, which emits a continuously changing background radiation.

3.1.1.3 Interferences

None reported. Spectra of air matrix were minimized by operating when a condenser across the electrodes was at a minimum capacity (250 micro-microfarads).

3.1.1.4 Accuracy, Precision and Stability

No specific data are reported for accuracy or precision.

Technique was not developed to a point where continuous quantitative measurements were made over periods involving many hours or days. Difficulties with electrode wear and mechanical and electrical instabilities were encountered.

3.1.1.5 Apparatus

3.1.1.5.1 Spectrograph - Quartz prism spectrograph (Hilger) with dispersion of 16 Å/mm at 2200 Å.

3.1.1.5.2 Excitation Source - Flow through spark chamber with quartz window; 1/4" lead-free copper electrodes; 12,000 volt transformer; condenser across electrodes adjusted to 250 micro-microfarads.

3.1.1.5.3 Detector Systems - Photographic plates or photoelectric Geiger counter.

3.1.1.5.4 Ancillary Equipment - Vacuum pumps, power supplies, electronic amplifiers, etc.

3.1.1.6 Time Cycle for Sampling and Measuring

Sampling and analysis time was approximately one minute with the direct reading system. Obviously, with the photographic plate technique, up to three hours could be required.

3.1.1.7 Calibration Procedure

Calibration was accomplished by measuring air containing minute amounts of tetraethyl lead. (Note - No specific data is given.) Chemical analyses of samples obtained from a common stream at identical times to the monitor were compared to the response of the monitor.

3.1.1.8 Method of Sampling and Sample Preparation

Air was drawn through Saran tubing to the spark chamber at 1 ft^3/min.

3.1.1.9 Multi-Element Application

Could be used on all metals. Authors specifically note Hg, As, Ba, and Be.

3.1.1.10 Physical Dimensions

None reported although total monitor was mounted on a wheeled carriage.

3.1.1.11 Unit Output

Milligrams Pb/ft^3.

3.1.1.12 Safety Hazard

Potential fire hazard presented by an open spark. However, later model was mounted in an airtight box in which an inert atmosphere such as nitrogen can be maintained.

3.1.1.13 Recommendations for Method Improvement

Newer grating spectrographs, photomultiplier tubes, and more stable power sources could add increased response and stability.

Use of electrodeless rf induced discharges as the excitation source could improve long term, continuous operation.

3.1.1.14 References

Aughey, H., "A Rapid Mobile Analyzer for Minute Amounts of Lead in Air," J. Opt. Soc. Am. 39, 292-293 (1949).

Koppius, O. G., "Detection of Lead in Air with the Aid of a Geiger-Muller Counter," J. Opt. Soc. Am. 39, 294-297 (1949).

3.2 Atomic Absorption Spectrophotometry

Measurements of lead content from ambient air, in particular air near alkyllead production facilities, have been made on a continuous basis by flame and non-flame atomic absorption techniques. With the flame technique, a detection level of 1 µg Pb/m³ was reached, whereas the non-flame method yielded a detection level of approximately 0.16 µg Pb/m³.

3.2.1 Flame Atomic Absorption Spectrophotometry

In general, the flame techniques use a hydrogen-contaminated air flame. However, some success has been attained by measuring the atomic absorption of lead in an argon 5 MHz induction plasma.

Thilliez (ref. 17,18) reports the detection of 1 µg Pb/m³ with a flame atomic absorption system which measures the Pb atoms in an open-ended tube after being generated in a hydrogen-contaminated air flame. The device is described for continuous monitoring of lead concentrations from tetramethyllead and tetraethyllead in the air of two workshops. Measurements are made at 2833 Å and the response time is less than two minutes. Its stability is demonstrated by the fact that its initial calibration has not required any modification during four years of operation.

In a somewhat similar system, but not applied to continuous monitoring of lead in air, Molden, et al. (ref. 19) attained increased sensitivity (10-fold) by using the 2170 Å Pb line, rather than the 2833 Å line. A hydrogen rich, air-hydrogen flame directed into a long path, low reflecting fused silica absorption tube was used to detect lead extracted from silicate rocks. By measuring the absorbance at 2170 Å and correcting for background absorption by subtracting the absorbance at the nonabsorbing Pb 2203.5 Å line, excellent calibration linearity was attained.

Ramirez-Munoz and Roth (ref. 20) also reported that the best single pass results for Pb were obtained with the 2170 Å line. In addition, they indicated that the 2614 Å Pb line may be useful for the extension of the dynamic range to higher concentrations.

Whenever the 2170 Å lead line is used, care must be taken to ensure that interference from copper materials does not occur. Hall and Woodward (ref. 21) have shown that erroneous results can be obtained if lead analyses are performed on samples having copper in the matrix. The error is due to the absorption by copper in the sample of copper radiation (2165.09 Å) emitted by the hollow-cathode lamp. The problem occurs with atomic absorption spectrophotometers which use slitwidths of 1 mm (nominal bandpass ca. 6.5 Å).

The effect would be eliminated if narrower slits were used; however, in many instruments the higher gain settings required when using narrower slits result in extremely high noise levels.

The difficulty can be eliminated by making measurements at 2833 Å or by using an electrodeless discharge tube as the energy source when measuring at 2170 Å.

A high-frequency (5 MHz) induction plasma (argon) was used in a reducing mode to vaporize powdered samples and to provide an absorption region (2 cm) for atomic absorption (ref. 22,23). Direct measurement of powdered samples for a number of elements including lead was accomplished. Higher sensitivity was attained in a reducing plasma than in a neutral plasma. No specific data are indicated, but good agreement with results obtained by flame spectrometry are reported.

The studies (ref. 22,23) demonstrate the possibility of a considerable increase in sensitivity while operating a plasma in the presence of reducing agents such as hydrogen. The sensitivity increase can be attributed to the direct reduction of metal oxides in the plasma or a delay in the oxidation obtained directly in the plasma by pyrolysis.

Verkhovskii, et al. (ref. 24) constructed an atomic absorption system without a monochromator by using high intensity lamps which emit narrow spectral lines and interference filters. Detection limits of 1.0 μg/ml with relative standard deviation of 30% for lead solutions are claimed. No data citing presence or absence of chemical or spectral interferences are reported.

A general study of the flame atomic absorption spectroscopy of lead was reported and experimental parameters were evaluated to optimize instrumental conditions (ref. 25). Operational conditions are indicated for several matrices including lead in air (lead trapped on iodine column and/or millipore filter). The most sensitive conditions were as follows: wavelength, 2170 Å; flame, oxy-hydrogen, with hydrogen atomizing the sample (reversed from normal); a "T" flame adapter. A detection limit of 0.013 ppm of Pb in aqueous solution is reported.

3.2.2 Non-flame Atomic Absorption Spectrophotometry

A very sensitive method (detection limit of approximately 0.16 $\mu g/m^3$) for the continuous measurement of lead in air was developed based on the reduction of lead compounds, particularly organo-lead compounds, over hot carbon. Atomic absorption measurements were performed on the Pb^o retained in a heated long-path absorption tube (ref. 26). The procedure is reported in detail in the following sub-section.

3.2.2.1 Atomic Absorption - Continuous Determination of Lead in Air

3.2.2.1.1 Principle and Applicability

3.2.2.1.1.1 Principle - Ambient air samples were analyzed continuously by drawing the air over hot carbon rods to reduce the lead compounds to the atomic state. The neutral atoms were passed into a heated long-path absorption tube where quantitative measurement of the Pb content was performed by atomic absorption spectrophotometry at 2833 Å.

3.2.2.1.1.2 Applicability - Method provided a rapid, sensitive, and reproducible system for the continuous determination of atmospheric lead. The lower limit of sensitivity was observed to be about 3×10^{-11}g of lead. Measurements were performed on laboratory air. No data are reported for field operation. Laboratory tests indicate that organic bound lead can easily be measured. Measurements on vapor emitted from externally heated lead phosphate, carbonate or chloride were also performed. However, no data are shown which define the problems related to handling lead oxide particulate directly.

3.2.2.1.2 Range and Sensitivity

3.2.2.1.2.1 Range - Approximately 0.16 μg/m³ to 54 μg/m³ in air, or as expressed on an absolute basis, 3×10^{-11}g to 1×10^{-8}g of Pb.

3.2.2.1.2.2 Sensitivity - Detection limit was estimated as 0.16 μg/m³ in air or on an absolute basis 3×10^{-11}g.

3.2.2.1.3 Interferences

3.2.2.1.3.1 Chemical - No interferences from most organic compounds (15 were tested) and water were observed. Halogen-containing organic compounds caused some change in the absorption intensity at the 100 mg/m³ (organic) level. Apparently some molecular absorption occurs.

Interferences caused by incomplete reduction of molecules to ground state atoms or the formation of refractory oxides or anion effects (PO_4^{3-} and CO_3^{2-}) commonly encountered with samples in aqueous media were not observed.

3.2.2.1.3.2 Physical - Radiation interferences were eliminated by using a modulated light source.

Particle size effects were not determined.

3.2.2.1.4 Accuracy, Precision and Stability

For ten samples containing a concentration of 6.0 μg/m^3 Pb, the maximum deviation from the mean was 4.5%, whereas the average deviation from the mean was 1.5%.

No data are reported for the length of time that the instrument was operated continuously. The consumption of carbon at white heat in an air stream may dictate only moderate continuous operation times.

3.2.2.1.5 Apparatus

3.2.2.1.5.1 Radiation Source - Demountable hollow cathode lamp using a shielded cathode and Jarrell-Ash 82-500 power supply.

3.2.2.1.5.2 Monochromator - Jarrell-Ash 82-500 1/2-meter monochromator - 100 micron fixed slits.

3.2.2.1.5.3 Detector - RCA 1P28 photomultiplier.

3.2.2.1.5.4 Carbon Reduction System - Four-inch graphite rods in quartz tubing heated with Lepel 5000 watt rf generator.

3.2.2.1.5.5 Absorption Tube - Quartz tube (160 cc) of unidentified length, heated by 1000-watt nichrome resistance heaters.

3.2.2.1.5.6 Ancillary Equipment - Compressor or vacuum pump, Jarrell-Ash 82-000 amplifier, Beckman Model 10005 Recorder.

3.2.2.1.6 Time Cycle for Sampling and Measuring

Continuous sampling and instantaneous measurement.

3.2.2.1.7 Calibration Procedure

Calibration of the apparatus was accomplished with a diffusion apparatus which introduced tetraethyllead from tubes of known diameter (approximately 1-10 mm) and path length. The rate of diffusion is determined by weight loss over a period of days or weeks. The response of the monitor was correlated with these diffusion rates.

3.2.2.1.8 Method of Sampling and Sample Preparation

Ambient air was introduced into the analyzer on a continuous basis with a small diaphragm compressor. Flow rate is approximately 1.2 liter/minute.

3.2.2.1.9 Multi-element Application

Although technique was applied only to lead measurements, the method could be modified to handle other volatile elements, e.g., Hg.

3.2.2.1.10 Physical Dimensions

No specifications reported. Estimated at 4' x 2' x 6'.

3.2.2.1.11 Unit Output

Absorbance values convertible to mass or mass/volume units.

3.2.2.1.12 Safety Hazard

Moderate to high temperature; some exposure to rf radiation.

3.2.2.1.13 Recommendations for Method Improvement

The effectiveness for converting lead compounds present in various particle sizes must be evaluated. The system should work well as an ambient air monitor, but residence times and conversion efficiencies, plus consumption rate of carbon rod reducing system, must be evaluated at higher air flow-rates for continuous stack emission monitoring.

3.2.2.1.14 Reference

Loftin, H. P., C. M. Christian, and J. W. Robinson, "The Continuous Determination of Lead in Air," Spectroscopy Letters 3, 161-174 (1970).

3.3 Atomic Fluorescence Spectrophotometry

Although atomic fluorescence spectrophotometry has not been applied to direct measurement of lead in air, the slightly lower detection limit (one-half that of flame atomic absorption) attainable with aqueous solutions suggests the possible application to air monitoring in selected cases. If, in a high copper matrix, the 217.0 nm line (Pb) cannot be used with the available instrumentation and, as a consequence, the sensitivity of the flame atomic absorption is insufficient, the atomic fluorescence measurements may be useful.

The experimental conditions for detecting low concentrations of lead by atomic fluorescence spectroscopy were studied and optimized (ref. 27,28). A detection limit of 0.01 μg/ml of lead in aqueous solution is obtained by measuring the direct-line fluorescence at 405.8 nm in an argon-oxygen-hydrogen flame. This detection limit is an improvement as compared to 0.02 μg/ml obtained by atomic absorption measurements at 217.0 nm (air-hydrogen flame) and 0.2 ppm by flame photometry at 405.8 nm (nitrous oxide-acetylene flame). The effect of 100-fold excesses of 30 cations and anions were examined, but only aluminum interfered significantly (43% drop in signal).

As noted above (ref. 27,28), low detection levels are attainable by atomic fluorescence spectroscopy (AFS) in aqueous media. However, consideration must be given to interatomic quenching of fluorescence, e.g., by nitrogen, if the AFS phenomena were to be applied to monitoring lead in air or in stack gas emissions introduced directly into the flame. Quenching of Pb fluorescence was observed (ref. 27,38) with an air-hydrogen flame. A 4-fold decrease in signal intensity was obtained with aqueous solutions in an air-hydrogen flame, as compared to an argon-oxygen-hydrogen flame.

3.4 X-ray Emission Spectroscopy

A number of excitation sources ranging from a Van de Graaff generator to the more common x-ray tube (tungsten target) and radio-isotope sources have been used to measure lead on air-borne particulate collected on filters. Although high sensitivities and attendant low detection limits result with the Van de Graaff system, devices using the latter excitation sources are more practical for field applications. In all cases, the techniques require the collecting of particulate for measurement. Also, the technique is restricted to particulate unless the lead vapor can be trapped by a complexing medium. (Note - The same complexing agents used in the colorimetric techniques for collecting lead vapor potentially could be applied to a paper tape sampling system using x-ray fluorescence detection principles.)

Detection limits of 1 microgram in airborne dusts have been reported (ref. 29-32) with x-ray tube excitation. Major problems are matrix and particle size effects. Also, direct spectral interference of the most sensitive lead lines L_{α} can occur with AsK_{α} fluorescent emission.

Cares (ref. 33) used x-ray spectrometry to measure lead in airborne metallic dusts and fumes collected on filter paper. A study of potential interferences, method of preparing reference standards, and x-ray characteristics of various types of filter media are presented.

Leroux and Mahmud (ref. 34) showed that air pollution samples collected on membrane filters and weighing less than 1.5 mg/cm^2 can be analyzed by x-ray emission spectrography without matrix correction for all elements with atomic numbers greater than manganese. The method is non-destructive, reaches detection limits to 0.05 μg/m^3, and requires about 5 minutes per element for analysis. Although glass fiber filters are not suitable for multi-element analyses due to presence of Ba, Sr, Rb, Zn, Ni, Fe, etc., both glass fiber filters and membrane filters can be used in Pb analyses. A comparison of the x-ray fluorescence results with atomic absorption measurements for the same samples shows a mean deviation between the techniques of 0.26 μg/m^3.

The x-ray emission (fluorescence) spectrographic method is rapid (5 minutes per element), but the time required to collect sufficient sample from ambient air is very long, up to 24 hours.

The analytical line (L_{α_1} - 1.1726 Å) generally used for measuring lead by x-ray emission or fluorescence techniques may be interfered with by the arsenic line (K_{α_1} - 1.1734 Å). Corrections can be made based on the ratio of the K_{α}/K_{β} lines of arsenic, if tungsten L_{γ} lines are not present. [Tungsten L_{γ} line group interferes with the arsenic K_{β} line (ref. 35).]

Buchanan and Schroeder (ref. 36) converted a single-channel x-ray spectrometer to a two-channel instrument to provide a means of recording lead x-ray fluorescence and background measurements simultaneously. The technique was devised to improve precision (minimize sample and electronic conditions) if long counting times (500 seconds) were used to attain high accuracy on trace quantities of lead on particulate collected from the atmosphere. The 420 plane of a lithium fluoride crystal was used to reflect background radiation while the 200 plane simultaneously reflected lead fluorescent emission. A maximum error of ±0.15 μg or 17% was observed at the 1 μg level.

Johansen, et al. (ref. 37) attained extremely low detection levels (0.3 ng) for lead from particulate collected by "dust fall" method on carbon foil from atmospheric air. For lead, L-radiation was generated by irradiating the sample in vacuum with a proton beam (MeV) from a Van de Graaff generator. Sufficient discrimination and sensitivity (counting times of 60 minutes) were obtained with a high resolution Si(Li)-detector to detect 0.3 ng Pb in the multi-element matrix characteristic of ambient air particulate.

Carr-Brion (ref. 38) compared the limit of detection for x-ray methods for on-stream analysis of a number of metals including lead in ores. The limit of detection was defined as percent element equivalent to 2 sigma background intensity with counting times less than or equal to 100 seconds and were reported as 0.001% for x-ray tube excitation and 0.004% for radioisotopic excitation. (Undoubtedly, the level of detection can be lowered at least by another order of magnitude with the use of semiconductor detectors.)

Enomoto (ref. 39) reported on a probe design for the continuous determination of Pb in aqueous solutions by using radioisotope γ-ray sources to induce x-ray fluorescence. A precision of 0.2% (absolute) was obtained for Pb in light matrices.

Portable x-ray fluorescence analyzers using x-rays produced by radioisotope sources were developed to detect lead and other elements having atomic numbers >20 (ref. 40). Fluorescence radiation is isolated by pairs of balanced absorption filters and the abundance of the metal in the sample is estimated from the difference count rate obtained when the two filters are used sequentially. Instrument weights were only 12 lbs and 16 lbs.

Burkhalter and Marr (ref. 41) report the detection limit of 40 ppm of Pb in synthetic standards and ores by using radioisotopic (^{57}Co) induced x-ray fluorescence.

Sciaraffa and Ziegler (ref. 42) sampled automobile exhaust emissions with a Millipore filter and then used a radioisotope-excited (^{109}Cd) x-ray fluorescence analyzer (Panalyzer-4000) to determine the amount of lead collected on the filter. With 64-second counting times, measurements of the L-lines of lead resulted in a detection limit of 5 μg of lead. However, in the presence of bromine, considerable over-lapping of fluorescence from bromine and lead was observed. To separate the lead signal, filters were required resulting in some loss of lead fluorescence intensity and moreover a minimum detection limit of 15 to 20 μg of Pb. [Note - Availability of newer, more efficient silicon (Li) semi-conductor detectors may permit better discrimination of lead fluorescence without filters and attendant loss of intensity.]

Hayashi (ref. 43) combined the use of x-ray fluorescent analysis and x-ray diffraction analysis to determine the quantity of lead and to establish the nature of the chemical composition of industrial lead fume collected on filter paper. The procedure was non-destructive. The limit of detection for lead (L_α line) was determined as 10 micrograms on a filter paper having a surface area of 99.95 mm^2.

A reasonable linear relationship was shown for lead content on the filter up to 50 mg of lead. There was no apparent variation with the limited particle size (0.3μ and 0.1μ) generated in a laboratory fume generator. Counting times of 180 seconds were used (ref. 43).

Cate (ref. 44) discusses the interference problems related to the determination of lead in air sample filters (Whatman 41) by isotope-excited, energy dispersive, x-ray fluorescence analysis. Spectral interferences of As, Pb, Br and Compton scattering from the isotope (^{241}Am) source are considered. By using ^{109}Cd excitation, although a less efficient exciter than ^{241}Am, and a high resolution semiconductor detector, a minimum detectable quantity of lead in a 10-minute count of PbL_{β_1} was 0.072 μg Pb/cm^2 (equivalent to 0.475 μg Pb for the 6.6 cm^2 filter disk used in the test). Cost of instrumentation was estimated by Cate (ref. 44) as $7,000-$8,000.

Rhodes, et al. (ref. 45,46) used ^{109}Cd to excite Pb to emit characteristic x-rays which were measured with a high resolution, semi-conductor detector. Particulate collected from ambient air for 24 hours on 8" x 10" Whatman 41 filter paper was analyzed for Pb and 16 other elements by using three different radioisotope sources. Direct analysis without corrections for matrix effects was possible by using thin specimens (average mass per unit area of 370 μg/cm^2). A detection limit of 0.11 μg Pb/cm^2 (0.025 μg Pb/m^3 of air) was attained with counting times of 10 minutes of the PbL_β emission. The major problem with the procedure is the need to equilibrate the cellulose filters for 24 hours in a constant humidity box before each weighing to minimize hygroscopic effects. In addition, weighing had to be performed for a fixed time (7 minutes) after removal from the box.

Qualitative identifications of the lead compounds were performed by x-ray diffraction measurements on samples containing 1.6 mg to 149 mg of lead. Generally, 2.8 x 4.8 cm sections were cut from the glass-fiber filter for the x-ray diffraction analysis.

3.5 Nuclear Activation Analysis and γ-Absorptimetry

Although activation analysis with thermal neutrons yields poor detection limits for lead, charged particle activation and irradiation with a fast neutron flux can allow lower detection limits. With fast neutron flux, 0.1% lead in a 100-mg sample can be measured.

A non-destructive neutron activation analysis method (ref. 47) was developed for measuring lead in Pb compounds and ores. The technique is applicable for emissions comprised principally of lead compounds. A detection of 0.1 mg of lead in a 100 mg sample is possible by irradiation with a fast (>5 MeV) neutron flux of 6 x 10^{11} neutrons/cm^2-sec for 20 minutes. After 30 minutes of cooling, $^{204}Pb^m$ is counted with a Ge(Li) semiconductor detector. Obviously this technique cannot be used as a field monitor, but does have potential application for laboratory analyses.

When lead is to be detected in an emission source which emits predominantly lead or lead compounds as particulate, γ-absorptimetry can be used for intermittent monitoring at moderate time intervals.

Strain and Leddicotte (ref. 48) measured lead in a variety of industrial samples by γ-absorptimetry with an ^{241}Am source.

Belina and Sotnikov (ref. 49) developed a γ-absorption method for automatic control of lead in ores, concentrates, and intermediate products. Since two γ-ray beams with different energies from ^{75}Se and ^{60}Co sources are used, the surface density need not be determined and corrections need not be made. The lead concentration is related to the ratio of the natural logarithms of the absorption of soft and hard γ-rays.

A rapid (3-4 min.) method for the determination of lead in finely ground, dried samples of Pb ore, concentrate, and tailings is reported based on γ-emission. The source of γ-ray emission is ^{133}Ba with a half-life of ~7.5 years. The apparatus is relatively stable, requiring recalibration once a month (ref. 50).

By measuring β-radiation backscattering phenomenon, a rapid (2 min.) determination of lead in lead products can be made. A ^{90}Sr (0.5m Ci) provided the β-radiation. The mean square error was reported as <0.3% absolute (ref. 51,52). (Note - Concentration range was not indicated.)

In a review of photon activation analysis, Lutz (ref. 53) indicates the application of the technique for non-destructive determination of lead using the reaction, $^{204}Pb(\gamma,n)^{203}Pb$. The principle advantage of the technique is the avoidance of the interference from ^{24}Na production encountered with thermal-neutron activation of materials, e.g., forensic samples, containing large amounts of sodium.

3.6 Colorimetric Methods

A number of manual colorimetric methods has been used to measure airborne lead collected in various media. Generally, these techniques are based on the formation of a colored complex with dithizone. High sensitivity provides a detection range of 1-500 μg Pb/m^3 of air. However, most of the methods require considerable time for collecting sufficient sample to detect the lead and additional time to prepare the specimens to develop the color-producing reaction.

Several relatively rapid methods using dithizone, tetrahydroquinone, tetrahydroxy-p-benzoquinone, and iodine have been applied to detecting volatile lead compounds in air. Although each may not be universally applicable, one or another might be usable in specific applications.

Moss and Browett (ref. 54) developed methods for determining particulate lead and tetra-alkyllead vapor in air by collecting particulate on a glass fiber filter and isolating the alkyllead in a hydrochloric acid solution of iodine monochloride. Measurements of lead-in-air concentrations down to 0.1 mg of lead per 10 cubic meters of air can be made automatically with the dithizone reaction and a Technicon Auto-Analyzer after sampling periods of 8 hours. An alternate method based on a sampling period of half an hour can provide a detection level of 0.3 mg of lead per 10 cubic meters.

Several color comparison methods, based on reaction of tetrahydroxyquinone (ref. 55,56), have been used to determine lead content in air. Also, Snyder, et al. (ref. 57) developed a rapid micromethod for field use based on a manual color development of lead, collected in iodine-potassium iodide solution, with a dithizone solution. The Snyder, et al. method requires approximately 10 minutes and is accurate to better than one microgram of lead per cubic foot of air.

The colorimetric methods could be modified for automatic colorimeters or for paper tape color comparison measurements.

A field test system for the determination of lead fumes in industrial atmospheres was developed based on the formation of a purple color on filter paper impregnated with tetrahydroxy-p-benzoquinone (ref. 58). After collecting the fume on the filter paper, the lead particles are dissolved in situ by means of a spray of glacial acetic acid and acetone. A uniform purple background stain is developed in a few seconds and quantitative measurements are made by comparing the color intensity with a standard color chart.

The method was developed specifically for determining lead fume (solid condensed dispersoids of particle diameter less than one micron and composed mainly of lead oxide particles) in the presence of moderate amounts of lead dust. The intent was to determine with reasonable specificity a type of particulate lead of well defined origin and size range, which also happens to be a particularly toxic form. Large particles of lead dust, which might be of relatively low toxicity, but could result in an analytical value far greater than the true lead fume concentration, are not measured.

The technique was applied to measuring lead fume in a lead-refining works and in a factory manufacturing storage batteries. Excellent agreement of the method was established with analyses performed by the dithizone and spectrographic methods on portions of the filter.

The method is sensitive to about 0.05 mg Pb/m^3. Above 0.2 mg Pb/m^3, the determination becomes less precise.

Of the common metal fumes, those of cadmium and zinc also form coloured complexes under the conditions of the field test. Antimony fume will form a color if more than the normal amount of spraying is carried out. The stains of these metals, when present in not more than moderate amounts, can be removed by washing with acetic acid or an aqueous solution of sodium hydrogen tartrate.

Although the method was developed for manual operation, an automatic paper tape system with photometric measurement of color could be developed for lead fume based on this approach.

Total airborne lead particulate collected on a paper filter has been determined by using an aqueous solution of tartaric acid-sodium hydrogen tartrate with glacial acetic acid and acetone spray to develop a characteristic color in conjunction with tetrahydroxy-p-benzoquinone (ref. 55).

The amount of volatile organic lead compounds in the atmosphere has been determined by passing a regulated stream of air over iodine crystals for a period of time so that at least one-half the iodine crystals are sublimed. Any PbI_2 compounds and free iodine are collected on a porous substrate. The free iodine is removed and a yellow color on the substrate indicates the presence of lead. By comparing the color with colors produced with known amounts of volatile organic lead compounds, quantitative measurements can be performed. The technique can be used to determine tetraethyl and tetramethyl lead in the atmosphere (ref. 59).

3.7 Electrometric Methods

An electrometric procedure based on anodic voltammetry was developed as a quick measurement of lead in atmospheric air (ref. 60). The technique is free from interferences and permits direct measurements of lead of the order of 0.02 μg. The collecting container is used as the electrolytic cell in the anodic voltammetric measurement. No data are given which would indicate the effect of compound type or physical form.

The application of square wave polarography as an automatic continuous analyzer of lead in the atmosphere is reported by Yamate, et al. (ref. 60). Sample air is passed through an absorbing bubbler containing 30 ml of 0.1N nitric acid for 46 minutes at 22 liters/minute. Subsequently, nitrogen is passed through the absorbing bubbler for 3 minutes to remove oxygen from the solution. The sample solution is transferred to an electrolytic cell. A high-sensitivity polarograph is programmed to record square-wave polarograms from -0.6 to -0.85 V. Wave heights of the recorded polarograms are converted to lead concentration ($\mu g/m^3$) by using prepared lead calibration curves. The detection range for Pb is reported as 0-15 $\mu g/m^3$. The procedure requires one hour. No data are reported for potential interfering materials.

3.8 Mass Spectrometry

Mass spectrographic techniques provide high sensitivity and specificity for manual analyses of lead in airborne particulate collected on filters. However, the need for a high vacuum during analyses and the time required to attain suitable conditions for efficient excitation precludes the application of this technique in a continuous monitoring system.

Brown and Vossen (ref. 62) used a special nitrocellulose filter and decomposition technique to measure lead (particulate) by spark source mass spectrometry. A detection range of 0.004-4 $\mu g/m^3$ was reported for lead collected in a batch sampling technique.

Matrix effects, resulting in problems related to proper preparation of standards to calibrate signal response intensities, are commonly encountered with ion- or spark-source mass spectrometry. To minimize these effects, a technique called isotopic dilution has been used. Although the technique is not applicable to continuous monitoring, the approach can be useful in selected cases for monitoring batch-type samples collected on filters.

Isotopic dilution techniques, when coupled with mass spectrometric measurements have been used to determine trace elements in many matrices (ref. 63). Generally, mass spectrometers with thermal ionization sources are employed, but are not suitable to simultaneous multi-element determinations. By using high voltage spark source excitation, all elements can be ionized (ref. 64).

Lead is isotopically altered, separated by cation exchange, eluted into an electrolysis cell, electrodeposited onto gold wire and sparked in the mass spectrograph. The method is somewhat involved and requires too much time for use as a monitoring technique.

Unlike most trace analytical methods, isotope dilution analysis does not require analyzed or synthesized standards of the same matrix material for reliable determinations. The simplest analytical procedure is to evaporate a portion of an isotopically spiked solution of the sample on a suitable substrate for sparking in the spectrometer. Compared to direct sparking of the sample, poorer limits of detection are obtained. In addition, unless separation techniques are used, a trace element may be undetermined if the only isotope lines suitable for measurement are interfered with by isotope lines of the matrix elements or complex ionized species of the matrix and polyatomic fragments.

Once equilibrium has been established with the added isotopes, the analysis is unaffected by sample losses.

For other special analyses, mass spectrometric analysis of volatile metal chelates can be used to detect ultra-trace (10^{-12}g to 10^{-14}g) lead (ref. 65). Because of the somewhat lengthy digestion procedures required to form the metal chelate, the technique would only be applicable to manual, intermittent, batch type analyses. The mass spectrometric measurement time is short, requiring <5 minutes.

3.9 Measurement of Ionization Current

The M.S.A. Billion-Aire (ref. 66) has been used to detect $PbEt_4$ (TEL) by forming particulate by sample pyrolysis and subsequent changes in current in an ionization chamber. With air in the ionization chamber, the finely divided particulate produces pronounced decreases in the current because the particles promote effective recombination of positive and negative ions by 3rd-body collisions and decrease the mobility of the ions. Most gaseous additives in concentrations of several thousand ppm cause only very small changes in the ion current. The technique permits the detection of alkyllead compounds down to the ppb level in air.

3.10 Detection of Lead Particles - Formation of Ice Nuclei

Although the universal application of this technique is questionable, restricted use is possible. Morgan (ref. 67) reported on a method for monitoring lead particles in the atmosphere by forming ice nuclei after reacting atmospheric lead with iodine. Continuous real time measurements were performed by counting the ice nuclei formed in the cold chamber of an acoustical counter.

Potential interferences are silver and terpenes which can also form ice nuclei with iodine.

Although the technique measures lead particles, rather than lead content, some consideration should be given to determine if the technique could be used to measure total lead content. By passing lead-containing air or stack gases through a thermal reduction process (flame or furnace heating) or reduction in CO (passage of lead-containing air over white-hot carbon), the elemental lead generated by reduction may be measurable by the ice-nucleating technique.

3.11 Gas Chromatography

Several methods have been developed to detect specific alkyllead compounds. Detection of these compounds on an intermittent, batch sampling basis is possible at the 0.02 μg/m^3 level.

Laveskog (ref. 68) reported the separation of tetramethyllead (TML) and tetraethyllead (TEL) from air by gas chromatographic means and detection with a mass spectrometer. By enriching the air samples, analyses of street air for TML and TEL were obtained between 0.02 and 0.2 μg/m^3. Approximately 10-15 minute sampling times are required for street air.

A gas chromatographic method using an electron capture detector has been used to measure tetraethyllead (TEL) down to 10^{-10}g/ml (or 100 ppb) (ref. 69). The method consists in passing the air for analysis at a flow rate of 1.5 liters/minute for 10-15 minutes through a sampling tube packed with the same material as the chromatographic column. The sample is subsequently desorbed and injected into the gas chromatograph. The concentration of TEL is determined from the values of peak areas and the specific retention volumes.

4. SUMMARY AND RECOMMENDATIONS

Although several techniques have been applied to the continuous monitoring of lead vapor, principally as the organo-lead compounds, no single method has been tested completely to qualify as a continuous monitor for total lead, i.e., vapor and particulate, from stationary source emissions.

Non-flame atomic absorption spectroscopy, preceded by a thermal and/or chemical reaction decomposition step to reduce airborne lead compounds to elemental lead and to maintain the elemental lead as vapor, should be considered. The major problems in adapting the most effective decomposition system (passage of air containing lead compounds over hot carbon) used for ambient air are: (a) efficiency of the reducing reaction at high stream velocities normally encountered in stack emissions and at the resulting short residence time in the decomposition zone is unknown; (b) potential plugging by refractory particulate in the carbon chamber when used with stack emissions involving high non-lead content, e.g., power plant fly ash, needs to be evaluated;

and (c) consumption of the hot carbon rods at high stack gas flow rates, where the stack gases are predominantly oxidants, e.g., oxygen, etc., must be determined.

Continuous monitoring of ambient air flowing at 1 ft^3/min. has been accomplished by emission spectroscopy with a spark discharge. The technique permits a working range of 0.003 mg Pb/ft^3 to 0.05 mg Pb/ft^3, but based on newer instrumentation may allow lower limits. The instrumentation was applied to measuring lead in vapor and particulate. Other methods of excitation - rf plasma, and intermittent arc - may also improve the efficiency of the emission spectrographic method.

X-ray emission (fluorescence) spectroscopy can be applied to measuring lead in particulate collected on filters. The major restriction to its application for determining total lead is its inability to analyze vapor. Some means must be found to collect volatile lead compounds on a filter-type media. Some consideration should be given to adapting paper tape samplers impregnated with complexing agents, e.g., tetrahydroxy-p-benzoquinone, used in collecting lead fume for colorimetric analyses.

When using the most sensitive lead line (L_α) for measuring lead by x-ray emission (fluorescence) spectroscopy, the analyst must be aware of potential spectral interference from As (K_α) in media containing moderate amounts of arsenic. The PbL_β line has been used successfully with ^{109}Cd radiosiotope excitation.

Techniques using γ-absorptimetry are not necessarily adaptable to universal measurement of lead but could be used in special circumstances where lead or its compounds would be the only compounds emitted and could be collected on filters, etc. The sensitivity of the method needs to be optimized and specific detection limits established.

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APPENDIX V

BRIEFING DOCUMENT - ANALYTICAL TECHNIQUES FOR ARSENIC AND ANTIMONY

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1. INTRODUCTION

Arsenic is emitted from stationary sources in a variety of chemical compounds. The most common arsenic compound is arsenic trioxide, which can be emitted as fume, vapor, or particulate. Smaller quantities of arsenic are emitted as the very volatile and toxic arsine. Arsenicals - inorganic and organic - used as herbicides, insecticides , defoliants and desiccants are present in stack emissions from production facilities and from plants, e.g., cotton gins, processing agriculture products.

No 24-hour maximum atmospheric concentration has been set for arsenic in the United States; however, the U.S.S.R. and Czechoslovakia use a basic 24-hour standard of 3 $\mu g/m^3$. The American Conference of Government Hygienists and the American Industrial Hygiene Association recommend threshold limit values for industrial workers (8 hour/day exposures) of 0.5 mg/m^3 for arsenic (ref. 1), 0.15 mg/m^3 for lead arsenate (ref. 1), and 0.2 mg/m^3 for arsine (ref. 2).

Antimony and its compounds can appear in stationary source emissions as the element antimony, as an alloy in combination with other metals, e.g., antimonial lead, or as the oxides, halides, sulfates and sulfides. The largest tonnage emissions occur in the ore refining processes where the predominant product is antimony trioxide.

The threshold limit values cited by the American Conference of Governmental Industrial Hygienists (1967) for antimony and its compounds (as antimony) are 0.5 mg/m^3.

2. SOURCES AND TYPE OF EMISSION

2.1 Arsenic and Its Compounds

Sullivan (ref. 3) reviewed the sources of emissions and uses of arsenic and its compounds. Arsenic, as arsenic trioxide, is produced as a by-product in gold and copper smelters. The low temperature (193°C) at which sublimation of arsenic trioxide occurs results in relatively wide-spread dissemination of the As_2O_3 as fume (vapor and suspended small particles). Arsenic trioxide is the predominant material used in the production of other arsenic compounds, and as a consequence, can be a major component in emissions from chemical production facilities.

Arsenic metal and arsenic compounds - arsenic sulfides, arsine, arsenic(V) oxides (in presence of a reducing agent) and organic arsenates - are readily converted by heat and oxygen to arsenic trioxide fume.

The volatile, toxic gas, arsine, is formed in pickling, soldering, etching, and plating processes where hydrogen is emitted from the dissolution of metals in acid. Organic and inorganic arsenicals are produced as agricultural chemicals and significant emissions have been reported from cotton gins.

Processes requiring the combustion of coal can produce measurable amounts of arsenic in the emission products.

Arsenic trioxide has a sublimation temperature of 193°C[1]; arsenic disulfide has a boiling point of 565°C. The halides, arsenic trichloride, trifluoride, and triiodide boil at 130.2°C, 63°C, and ∿400°C, respectively. Arsine has a boiling point of -55°C, and lead arsenate decomposes above 280°C. Elemental arsenic sublimes ca. 600°C and has a vapor pressure of 1 mm at 372°C.

2.2 Antimony and Its Compounds

The natural and industrial sources of antimony and its compounds, and the chemical and physical properties of the various antimony compounds are described in a series of review articles (ref. 4).

Antimony trioxide (sublimation temperature of 1550°C) is generated as the major antimony compound in ore refinery processes. Sublimation of the trioxide is used for separating antimony from the ore. Antimony trioxide is a chemical intermediate, flameproofing agent, and an additive in ceramic, glass and paint manufacturing.

Halides - $SbCl_3$ (b.p. 223°C), $SbBr_3$ (b.p. 280°C), and SbI_3 (b.p. 401°C) - are chemical intermediates and are used as mordants and catalysts, and in the electroplating industry.

Antimony trisulfate and pentasulfide decompose when heated and are used in manufacturing explosives, fireworks and other pyrotechnics. The pentasulfide is also used as a pigment and in vulcanizing rubber. The trisulfide is a good camouflage pigment and is used with the pentasulfide in matches.

Antimony oxychloride decomposes at 170°C and is used as a chemical intermediate and as a smoke-producing agent.

Footnote:

[1] The vapor pressure of arsenic trioxide varies considerably depending on the crystalline or amorphous form - monoclinic, octahedral, and glassy. Typical vapor pressure data are: 2.4×10^{-7} mm @ 60°-61°C; 2.5×10^{-5} mm @ 81°-86°C; 4.6×10^{-4} mm @ 101°-105°C; 2.2×10^{-3} mm @ 119°-126°C; and 2.6×10^{-2} mm @ 149°-152°C.

The very volatile and toxic stibine (SbH_3 - b.p. -17°C) is produced by the reaction of hydrogen on antimony or its compounds.

Alloys of antimony are used as bearing metals, battery plates, cable coverings, and castings. The chief alloys are brittania metal and antimonial lead.

3. CANDIDATE ANALYTICAL TECHNIQUES

No direct reading instruments for field application are available for measuring arsenic and antimony in ambient air or in stack emissions. Laboratory methods are based on the collection of dust or fumes with filter paper samplers, electrostatic precipitators, and/or impingers.

Analytical techniques relying on instrumental methods have been applied to measure arsenic and antimony in various media, including particulate collected from ambient air. The techniques used predominantly are colorimetry, iodine microtitration, atomic absorption spectrophotometry, atomic fluorescence, emission spectroscopy, x-ray fluorescence and neutron activation analysis. Most of these methods are based on analyses of particulate collected on filters (paper or glass fiber) and suffer from the high probability of potential loss of vaporized As_2O_3 and other compounds when large volumes of air are drawn over the collected particulate. Some of this loss can be minimized by a tandem arrangement of filter and impinger containing a collecting liquid. The vaporization losses on filters could be moderately high when sampling heated stack gases.

3.1 Colorimetry and Microtitration

3.1.1 Arsenic

Determinations of arsenic are performed by reaction with silver diethyldithiocarbamate (ref. 5,6), by iodine microtitration method using an amperometric titrator (ref. 7), and by reaction with molybdenum blue (ref. 8).

The Gutzeit method (reaction with mercuric chloride or bromide) (ref. 6) is not recommended, except for laboratories where a very large number of analyses is performed (ref. 6). The Gutzeit method is susceptible to changes in many variables.

Conversion of the arsenic compounds to arsine is required in the molybdenum blue, silver diethyldithiocarbamate, and Gutzeit methods. To obtain conversion to arsine, the arsenic must be in the trivalent state. Each method, therefore, incorporates a reduction step to ensure total conversion to the trivalent arsenic. Antimony may result in an interference as stibene in amounts in excess of 0.0001 g. Hydrogen sulfide, unless removed by the lead acetate glass wool plug in the standard train, can also interfere.

The formation of arsine is based on the reaction of trivalent arsenic with nascent hydrogen generated by reacting zinc metal with sulfuric acid. Since oxygen inhibits the formation or arsine, air should be eliminated. The reaction is a batch process. A detailed study of the interferences encountered with the evolution of arsine was reported by Whitnack and Martens (ref. 9). Interferences were observed when ppb quantities of chromate, molybdate and metavanadate ions were present. Slower rates of hydrogen evolution were observed and the formation of molybdenum and vanadium arsenite complexes are suggested. Additional interferences of nitrates, chlorates, or compounds of copper have been observed (ref. 10).

The silver diethyldithiocarbamate is the most sensitive and simplest of the four methods for arsenic. By collecting a specimen from ambient air at 1 ft^3/min. using water or decinormal sodium hydroxide as collecting medium in a Greenburg-Smith impinger, a detection limit of approximately 0.1 to 0.2 μg arsenic per cubic meter, in a 30 cubic foot air sample, can be attained (ref. 5,6).

Agranov (ref. 11) reports the development of an automatic gas analyzer which permits the detection of arsine and arsenic at the 1 mg/m^3 level (estimated). No specific details are given, but the general approach is to measure the change in the light absorption in the reflection by a paper tape, on which a color reaction is developed.

3.1.2 Antimony

Several volumetric methods (a) $KMnO_4$, (b) $KBrO_3$, (c) I_2 have been used to titrate Sb(III) (ref. 12). Interferences by As(III), Fe(II), SO_2, V(IV) occur. Two colorimetric methods, rhodamine B and iodoantimonous acid, have found favor for estimating trace quantities of antimony (ref. 12). An, Fe(III), Ga, Tl and W can interfere in the rhodamine B method. Bi and Tl can interfere in the iodoantimonous acid method.

Traces of antimony may be detected by evolution of stibine that forms when antimony solution is treated with zinc and hydrochloric or sulfuric acid, and by measurements with one of the colorimetric techniques indicated above (ref. 12).

3.2 Atomic Absorption Spectrophotometry

3.2.1 Arsenic

Arsenic has been measured with a variety of atomic absorption techniques. By varying flame composition - air-acetylene (ref. 13,14), argon-hydrogen (ref. 12), nitrous oxide-acetylene (ref. 15), oxy-acetylene (ref. 16) - high flame background and noise levels obtained at the resonance lines, 193.7 nm or 196.0 nm, can be minimized. These techniques are based on measurements with aqueous solutions of arsenic and yield detection limits of approximately 1 ppm of arsenic in water.

Thompson et al. (ref. 17) reported the detection limit of 0.02 μg As/m^3 of air by atomic absorption spectrophotometric measurement of acid solutions of particulate collected on glass fiber filters (based on 2000 cubic-meter air sample). Sample collection and sample digestion and analysis require relatively lengthy time periods.

Ando, et al. (ref. 18) improved the sensitivity by using a nitrogen (entrained air)-hydrogen flame in conjunction with long-path (91 cm) Vycor cells. A detection limit of 0.006 μg of As per ml of solution (H_2O) is claimed. Major improvements in minimizing flame absorption are attained. Interferences are many: (a) all acids as well as ammonia affect absorption of arsenic at 1937 Å, (b) magnesium, calcium, aluminum, nickel, cobalt and manganese reduce arsenic absorption (attributable to formation of arsenides in the flame), and (c) increasing concentrations of iron first increase and finally decrease arsenic absorption. Even in very high reducing environments (hydrogen) dissociated neutral atoms of arsenic combined with oxygen to form white deposits of arsenic oxide on the cell wall causing serious changes in sensitivity. Cells had to be cleaned often.

By generating arsine, Holak (ref. 19) was able to detect 0.04 μg of arsenic by atomic absorption spectrophotometry.

The arsine generator technique has been used in colorimetric methods, but is also currently being promoted as a means of increasing the sensitivity of atomic absorption spectrophotometric measurement for arsenic. Sampling systems for generating arsine for delivery to the atomic absorption spectrophotometer are available commercially from Perkin-Elmer Corp. and from Fisher Scientific Co. (Jarrell-Ash Div.). The basic apparatus and principles are described by Fernandez and Manning (ref. 20) and Manning (ref. 21). An absolute detection limit of 0.02 μg is reported; arsine generation requires 4-5 minutes.

Folger, et al. (ref. 22) reported the development of an arsine generating system using concentrated hydrochloric acid, instead of sulfuric acid, and using a large surplus of fine-grained zinc powder to a small volume of solution. By operating at room temperature, 90% of the arsine [10 μg As(III)] was generated in one second and 99.8 ± 0.2% was produced in one minute.

3.2.2 Antimony

Yanagisawa et al. (ref. 23) studied the determination of antimony in different flames and found that the acetylene-air flame was most suitable. They found no interferences from other cations or anions.

The 2176 Å wavelength is generally recommended. A sensitivity of ca. 1 μg/ml can be attained and a copper interference is noted (ref. 24).

Stresko and Martiny (ref. 25) report a negative effect by Cu and an enhancement by Pb when the most sensitive line, 2176 Å, is used with a 7 Å slit. The lead interference is not observed with a 2 Å slit. Apparently the interference is due to the absorption of an antimony line at 2170.23 Å by the primary lead line at 2169.994 Å (ref. 26). It is worthy to note that the opposite effect of antimony on a lead determination does not appear.

3.3 Emission Spectroscopy

Very little data are reported for flame-, arc-, or spark-excited emission spectrographic analysis of arsenic and antimony. Poor detection levels are generally reported. Dean and Carnes (ref. 27), and Dean and Adkins (ref. 28) show that emission lines for elements of high excitation potential and high ionization potential, that are generally absent or very weak in the portion of the excitation zone (e.g., mantle of a flame) generally used for analyses, appear with unusual strength in the spectrum of the reaction zone (e.g., rich acetylene-oxygen flame). Emission intensity can be enhanced in the flame by using organic aerosols, and continuous background radiation from the reaction zone can be minimized by using a light-guide.

In measuring solutions with flame emission spectroscopy, detection levels of 2.2 μg As/ml and 1.0 μg Sb/ml are reported (ref. 27). Some spectral interferences are observed but have been minimized by selecting other analytical lines. The 228.8 nm arsenic line suffers direct interference from the cadmium line at 228.8 nm and the tin line at 228.7 nm. The tin line at 235.5 nm and the nickel line at 234.5 nm could interfere with the arsenic line at 235.0 nm if the slit width ever exceeded 0.3 mm. Concentrations of antimony, up to at least 500 μg/ml, did not affect arsenic. However, arsenic depressed the emission of antimony by approximately 2 μg/ml (out of 80 μg Sb/ml) for each 100 μg As/ml. Tin at concentrations of 1000 μg/ml did not affect arsenic, but zinc repressed arsenic by approximately 1% per 100 μg Zn/ml.

The use of radio-frequency induced emission spectroscopy requires additional investigation. Dickinson and Fassel (ref. 29) show detection limits in rf plasma emission of 0.1 μg As/ml and 0.2 μg Sb/ml.

No data are available for continuous, flow-through, emission studies on airborne arsenic and antimony. However, modification of techniques reviewed in other documents in this series,

(a) beryllium and cadmium, (b) mercury, and (c) lead, and reported elsewhere (ref. 30,31,32,33,34) should be considered.

3.4 Atomic Fluorescence Spectroscopy

Dagnall, et al. (ref. 35) developed an analytical technique for antimony in aqueous solutions using atomic fluorescence spectroscopy. Atomic fluorescence measurements at 2176 Å permits the determination of antimony in the range 0.1-120 ppm with a detection limit of 0.05 ppm. With the same equipment and source, the range of measurement for atomic absorption was 6-120 ppm and the detection limit was 1 ppm. No interferences were observed from 100-fold molar amounts of Cd, Cu, Co, Fe, Hg, K, Mg, Mn, Mo, Na, NH_4, Pb and Zn or from arsenate, chloride, nitrate, phosphate and sulfate.

3.5 X-ray Emission Spectroscopy

Excitation of secondary emission (fluorescence) of x-rays can be induced by a number of excitation sources including electron beams, higher energy x-rays, or alpha, beta, and gamma radiation from radio-isotopic sources. Very little information on the application to determination of arsenic and antimony in airborne particulate is available. Analyses have been reported in a variety of liquid and solid matrices; detection of 1-10 μg of arsenic can be attained with conventional x-ray spectrometry (platinum target x-ray tube). The technique is limited to analyses of particulate collected on filters and is not applicable to continuous monitoring. The technique is also subject to matrix and particle size effects.

3.5.1 Arsenic

The measurement of trace quantities of arsenic in a matrix containing low to moderate proportions of lead are not possible. Two effects are noted: (a) high absorption properties of the matrix (moderate to high quantities of lead), and (b) spectral interference of the Pb $L\alpha_1$ (1.173 Å) line with the As $K\alpha_1$ (1.173 Å) line. Determinations of arsenic in antimonial lead alloys can be made in the range of arsenic contents, 0.05%-0.06%, by using the weaker $K\beta$ lines for arsenic (1.057 Å) (ref. 36). Care must also be taken to minimize the background radiation interference from the x-ray tube with the arsenic analytical lines, particularly $WL\gamma_3$ with As $K\beta_1$ (ref. 37). Primary beam filters are useful to a certain degree but some attenuation of the analytical line can be experienced (ref. 37).

3.5.2 Antimony

Antimony ($K\alpha$ 0.472 Å) has been measured in lead alloy matrices (antimonial lead) (ref. 36) and in presence of Sn, Se, As, Ge, and Cu (ref. 38). The high proportion of lead affects the absorption of both primary and secondary x-rays resulting in only moderately low detection limits. However, limits of detection of 2 micrograms are attainable in other matrices (ref. 38).

3.6 Neutron Activation Analysis

Nondestructive neutron activation analysis has been used to measure airborne arsenic and antimony collected as particulate on filters near several metropolitan areas. Although high sensitivity can be attained, long cooling times or separation techniques are required to minimize interferences.

3.6.1 Arsenic

Nondestructive measurement of arsenic in airborne particulate by neutron activation analysis was reported by Dams, et al. (ref. 39). Detection limit of 0.04 μg or 0.004 $\mu g/m^3$ in a 24-hour sample are attained. This detection level is attained by irradiating with thermal neutrons for five minutes, waiting 20-30 hours for cooling and counting for 2000 seconds. The long cooling time is required to minimize interferences.

Rudelli et al. (ref. 40) reports on a variety of interferences involved in the application of NAA to determine arsenic and antimony. It is important to realize that care must be taken to have sufficient resolution and to understand the potential interferences. Limitations for the nondestructive activation analysis of both arsenic and antimony can be minimized by using Ge(Li) spectrometers. It is notable, that in some samples where the antimony content is high, arsenic was not detected.

A rapid and non-destructive fast-neutron activation analysis using a semiconductor detector (ref. 41) was developed which would permit a sensitivity of 10-100 μg/10 counts for arsenic after irradiation of selected samples for 400 seconds. The method was proposed for industrial quality control.

3.6.2 Antimony

Rudelli, et al. (ref. 40) applied nondestructive activation analysis to measuring arsenic and antimony in high tin matrices. A problem arises from the contribution to the antimony content by the matrix, even when chemical separation has been conducted. This is due to the presence of ^{125}Sb produced by the reaction $^{124}Sn(n,\gamma)^{125}Sn \xrightarrow{\beta-} {}^{125}Sb$. The energy of the gamma rays of ^{125}Sb is very similar to the energy of gamma rays of ^{122}Sb and ^{124}Sb, both produced by n,γ reaction from natural antimony. The best NaI(Tl) crystals do not provide sufficient resolution. Also, the presence of arsenic causes a serious interference because the photopeak of ^{76}As at an energy of 559 keV cannot be resolved from the 564 keV peak of ^{122}Sb with the NaI(Tl) crystals. In addition, unless sufficiently long cooling times are used, interferences can also be observed for copper, iron, zinc, silver and sodium. All interferences can be eliminated by using higher resolution Ge(Li) spectrometers.

Fujii et al. (ref. 41) developed a rapid and nondestructive fast-neutron activation analysis technique for a number of elements including antimony by using a co-axial Ge(Li) semiconductor detector. Based on irradiation times of 400 seconds and recording times of 500 seconds, antimony was detected with sensitivities of <10 μg/10 counts.

A number of neutron activation analyses of airborne particulate has been reported (ref. 42,43). Detection levels of antimony in particulate collected on filters (cellulose) in the Chicago area range from 1.4 ng/m^3 to 55 ng/m^3 (ref. 43). With decay times of 20-30 days and collection times of 24 hours, the minimum detectable concentration of antimony in urban air was 0.001 μg/m^3 (ref. 39). Haines et al. (ref. 44) used an automatic smoke sampler and neutron activation analysis to detect airborne antimony oxide. Background interference from soot and filter paper limited the technique to about 0.2 micrograms of antimony without separation procedures.

3.7 Mass Spectrographic Analysis

The sensitivity of the mass spectrometric method is dependent in large part on the means by which the sample is excited. Very poor efficiencies are encountered with thermal ionization of arsenic. The needed high sensitivity and selectivity for metals are attainable only by ion- or spark-source mass spectrometric techniques. However, analyses must be performed in a relatively high vacuum and, as a consequence, the measurements are made on a batch basis and require considerable time between samples to attain suitable conditions for efficient excitation. The technique is limited to measuring samples collected on a filtering device and is not applicable to direct and continuous source monitoring.

Due to the relatively high volatility of As_2O_3 and other arsenic compounds, considerable error can be encountered due to losses with high volume air sampling filters, digestion or sample preparation steps, and pumping down to the necessary vacuum.

Brown and Vossen (ref. 45) report the measurement of arsenic (0.005 μg/m^3) in air pollution particulates collected on a special nitrocellulose filter pad. Total analysis time, including combustion of the filter and preparation of the graphite electrode, required approximately 2-1/2 hours per sample.

By using a special modification of a thermal ionization source which allows an electron bombardment crucible source system to be used in thermal ionization solid source mass spectrometers, a detection level of less than 5 µg antimony in solid specimens is possible with low memory effect (ref. 46).

4. SUMMARY AND RECOMMENDATIONS

There is no technique available for measuring arsenic and antimony continuously in ambient air or in stack emission. All techniques presently used in measuring the air pollutants - arsenic and antimony - require the collection of particulate in impingers or on filters.

The low sublimation temperature of As_2O_3 suggests the potential loss of volatile arsenic compounds from particulate collected on high volume filtering systems. Analytical techniques, e.g., x-ray emission (fluorescence) spectroscopy, neutron activation analysis, and mass spectroscopy, using this method of collection may yield low results.

Similar low results will also be observed with emission spectrographic techniques based on analyzing particulate collected on filters. However, emission spectrographic techniques based the excitation of a continuous flowing stream of air or stack gas through an excitation zone would not have this problem.

Other than using flame (acetylene-oxygen), or radio-frequency induced excitation of flowing solutions of arsenic and antimony, no data are available regarding spectrographic analyses of flowing air samples. Based on information derived from flame excitation studies, a moderate amount of development work should be anticipated to establish the optimum viewing zone in the flame or plasma. Emission lines of elements (arsenic and antimony) of high excitation potential and high ionization potential may not appear in the flame mantle, but occur as intense emission lines in the reaction zone under the proper conditions. The use of radio-frequency or microwave-induced plasmas should be considered. The latter when used in a low power mode will not permit direct measurments, but will require isolation of the arsenic or antimony in impinger solutions.

Considerable difficulty can be experienced in attempting arsenic analyses in high lead matrices by x-ray emission (fluorescence). Not only does the high absorption characteristic of the matrix cause problems, but direct spectral interference of Pb $L\alpha_1$ radiation occurs with As $K\alpha_1$.

When using neutron activation analysis, particularly as a nondestructive technique, instrumentation having high resolution capability [Ge(Li) semiconductor detector] is necessary to minimize a variety of interferences in measuring arsenic and antimony in stack emission particulate.

The use of an arsine generation step aids in concentrating arsenic for atomic absorption spectrophotometry, colorimetry, and potentially flame-, rf- or microwave-excitation of emission spectra, but the total analysis time requiring collection of sample, digestion to yield trivalent arsenic, and generation of arsine is too long for short-term, intermittent measurements.

Although a long path absorption tube improves the sensitivity of the atomic absorption method for arsenic, considerable interferences (formation of arsenides, oxides) can occur, resulting in low arsenic measurements. High flame or non-flame temperatures are needed.

Considerable development work is needed to attain continuous monitoring of arsenic and antimony from stack emissions. The most promising approaches are based on direct measuring of emission spectra generated by an arc excitation or by a radio-frequency plasma.

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APPENDIX VI

BRIEFING DOCUMENT - ANALYTICAL TECHNIQUES FOR BARIUM, BORON, CHROMIUM, COPPER, MANGANESE, NICKEL, AND VANADIUM

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1. INTRODUCTION

Information related to the technology for continuous measurement of barium, boron, chromium, copper, manganese, nickel and vanadium in emissions from stationary sources is presented in this report. There are no continuous monitors currently available which will measure these elements individually in all the physical and chemical forms found in stationary emission sources.

Data on physical and chemical properties of each element and its compound are reported to show potential problems regarding the physical state and reactivity of specific emissions. Although little information is available regarding continuous monitoring, selected references are summarized to indicate the potential application of certain analytical technology and limitations of other analytical methods for continuous measurement of the emissions from stationary sources.

2. SOURCES AND TYPE OF EMISSION

2.1 Barium and Its Compounds

The major industrial sources of barium emissions are the processes involved in the mining, refining, and production of barium and its compounds (ref. 1). Quantitative data on the amount of emissions from industrial processes are not available.

The two main barium-containing minerals are barite (barium sulfate) and witherite (barium carbonate). Of the two minerals, barite is the principal mineral used in the United States. Barium compounds are also found in the waste (gangue) in lead and zinc ore deposits and in most igneous rocks.

Barium oxide is reduced with aluminum powder to produce barium metal which is recovered from the reaction retort by distillation at 1200°C at approximately 0.1 mm. Barium metal is very reactive and is used to remove residual gases in radio tubes and to produce barium-nickel and lead, barium and calcium alloys.

Barite (barium sulfate) is used for oil-drilling muds, as filler in paper, cloth, etc., as the white paint pigment, lithopone, as raw material for producing barium compounds, and as a component in glasses, glazes and enamels. Lithopone - 70% barium sulfate and 30% zinc sulfide - is used as a pigment and is also used in manufacturing of automobile tires, rubber matting, and other rubber products.

Barium sulfide is produced during the reduction of barium sulfate with coal and serves as the raw material for other compounds. Barium carbonate produced by CO_2 or carbonate reaction with the sulfide is an intermediate in preparing other barium compounds. The carbonate is used in ceramic and glass industries; in preparing case-hardened steels; and in manufacturing photographic paper.

Barium chloride is the most important of the halides and is prepared by reacting BaS with hydrochloric acid to yield the chloride salt and hydrogen sulfide. The chloride is used as a chemical intermediate, as a filler, and in steel carburizing. The bromide is a raw material for preparing phosphors and the fluoride is used as a flux and opacifier in enamels and is used in glass manufacture.

Barium nitrate is used in pyrotechnics, in green flares, in tracer bullets, in primers and in detonators.

Barium oxide has a high reactivity to water and carbon dioxide and readily forms the hydroxide and carbonate. The oxide is formed by heating the carbonate with carbon in a brick kiln or electric-arc furnace. The oxide is used as an intermediate in producing barium hydroxide and barium peroxide. Other uses include formulation of lubricating oil detergent, glass manufacturing, and as a desiccant for refrigerants in household refrigerators.

Barium stearate is utilized as a metallic soap and drier. Barium acetate and barium benzene sulfonate are lubricating oil additives. Also, the acetate is a mordant for printing fabrics and a catalyst for organic reactions.

Barium chromate is a pigment in coloring glass, ceramic and porcelain and is used in metal primers, pyrotechnics and safety matches.

The combustion of coal is an additional source of barium emissions. The barium content in coal ash ranges from <0.1% to 4%.

Barium chloride boils at 1560°C; barium fluoride has a boiling point of 2137°C. Barium oxide melts at 1923°C and boils around 2000°C. The carbonates, nitrates, and hydroxides decompose to the oxide on heating.

The Threshold Limit Value (TLV), recommended by A.C.G.I.H. in 1967 for 8-hour occupational exposure to soluble compounds of barium in air, is 0.5 mg/m^3.

2.2 Boron and Its Compounds

Durocher (ref. 2) divided the compounds of boron into six general groups: (1) boron oxides, boric acid, and borates; (2) boric acid esters; (3) refractory boron compounds; (4) boron halides; (5) boron hydrides; and (6) organic boron compounds.

Borax and boric acid have the greatest commercial applications of the Group 1 compounds. Boron dusts of unknown composition (probably mixed oxides) are emitted in iron furnaces. Limited data indicate a boron concentration of approximately 0.05% in particulate from a gray iron furnace (ref. 2). Boric acid is used as a ceramic glaze, chemical intermediate, alloying material for steel, antiseptic, flameproofing agent, cosmetic base, and dye stabilizer, and is used in electroplating solutions, in photography, and in latex paints.

Borax serves in manufacture of glasses and ceramics; in leather-tanning industry; in detergent and soap formulations; in cosmetics. It is also an effective preservative and fire retardant; aids in controlling microorganisms in fuels and solvents; and is an ingredient in artificial fertilizers. Sodium tetraborate pentahydrate serves as a rust inhibitor in antifreeze solutions, as an ingredient in liquid starches and as an intermediate in preparing other borates. Ammonium biborate is used in manufacture of organic resins; ammonium pentaborate is used in electrolyte condensers.

The boric acid esters (Group 2 compounds) are produced by esterification of boric acid with alcohols or phenol or by reacting boric oxide with alcohols. The esters serve as fuel and lubricant additives, as antiknock agents in gasoline (most important of all uses), as growth inhibitors for microorganisms in diesel and aviation fuels, as anti-icing agent, and as an anti-oxidant. Other uses include epoxy resin curing agent, nuclear-shielding, and components in nuclear-detecting devices.

The Group 3 refractory boron compounds include metal borides, boron carbide, and boron nitride. The metal borides generally contain one or more of the following elements in combination with boron: aluminum, chromium, nickel, calcium, barium, manganese and copper. The borides are used primarily in rocket engines, jet turbines, and other equipment subjected to high temperatures and chemically reactive agents. Boron carbide serves as an abrasive, in jet engine parts, and as a semiconductor. Boron nitride is used in manufacture of heat resistant materials and for high-voltage electrical insulation.

The boron halides of Group 4 include the trichloride, trifluoride, tribromide, and triiodide compounds. In addition, the trifluoride combines with the fluoride ion to form fluoborate ion, BF_4^-, which, in turn, can combine with cations to yield the fluoborates, e.g., $NaBF_4$. The halides, BF_3 and BCl_3, are useful as catalysts; all trihalides of boron hydrolyze readily.

Boron hydrides, boranes, which comprise the Group 5 compounds are represented by two generic formulae: B_nH_{n+4} and B_nH_{n+6}. The most important are the compounds in the first series where n = 2, 5, 6, and 10, and in the second series where n = 4 and 5. Diborane is a toxic gas that readily ignites in moist air; diborane is used as a polymer catalyst and in manufacture of higher boranes and amine complexes. Higher boranes are used as high-energy fuels. Decaborane is the most stable borane and is used in vulcanization of rubber and as a fuel for rockets.

Boranes also form metal borohydride or hydroborates with metals. The general formula is $M(BH_4)_x$, where x may vary from 1 to 4 depending on the metal atom. Typical compounds are $LiBH_4$, $NaBH_4$, $Be(BH_4)_2$, $Al(BH_4)_3$, $Ga(CH_3)_2$-BH_4, $Mg(BH_4)_2$, $Ca(BH_4)_2$, $V(BH_4)_4$, and $Zn(BH_4)_2$.

The boranes also react with amalgams of the highly electropositive metals to form addition products - $Na_3B_3H_6$, $K_3B_4H_{10}$, and $K_2B_5H_9$.

Polymerization of borazole, produced by reacting borane and ammonia, yields a long-chain polyphenyl-type product.

Group 6 compounds are produced by replacing hydrogen atoms of the boranes with alkyl or trimethyl amine groups. Little information is available regarding the commercial importance and production figures for these compounds.

The combustion of coal is an additional source of boron. Concentrations of approximately 0.005 to 0.2% of boron have been found in ash from various grades of coal.

Boron boils at 2550°C and boron oxide has a boiling point of 1500°C. Boron nitride sublimes at 3000°C, whereas the trihalides, BBr_3, BCl_3, BF_3, and BI_3 boil at 90.1°C at 740 mm, 12.5°C, -10.°C and 210°C, respectively. The boranes are very volatile; typical boiling points are: diborane, -92.5°C; pentaborane, 0°C at 66 mm; decaborane, 100°C at 19 mm; and trimethylborane, -20.2°C. Trimethyl borate boils at 68.7°C.

The Threshold Limit Values (A.C.G.I.H.-1967-TLV) are boron oxide, 15 mg/m^3; boron trifluoride, 3 mg/m^3; diborane, 0.1 mg/m^3; pentaborane, 0.01 mg/m^3; and decaborane 0.3 mg/m^3. Although no TLV has been established for boric acid, Hyatt and Milligan (ref. 3) suggest that the concentration not exceed 2 mg/m^3.

2.3 Chromium and Its Compounds

Chromium emissions can occur in the metallurgical and chemical industries, in chrome plating, in processing asbestos, in manufacturing cement, and in burning coal (ref. 4).

The only important commercial chromium mineral is chromite which has the general chemical formula $FeO{\cdot}Cr_2O_3$ where MgO (4-15%) can replace some FeO (11-20%) and portions of the Cr_2O_3 (42-55%)

can be replaced by Al_2O_3 (7-16%). CaO (1-5%) and SiO_2 (3-8%) may also be present. Chromite used in the metallurgical industries is usually converted into ferrochromium or chromium alloyed with iron, nickel, or cobalt. Most of the chromium is used in making stainless steel, other specialized steels, and nonferrous alloys.

Because of its chemical inertness and high melting point (∿3956°F), chromium ore is used to manufacture refractory bricks and as coatings to close pores or join furnace bricks.

Sodium chromate, produced directly by roasting chromite ore with soda ash or soda ash and lime, and sodium dichromate are the principal chemicals from which other chromium compounds are prepared. The monochromate ion exists in alkaline solution and the dichromate in acid solution. In preparing the chromate, trivalent chromium dusts are emitted from dry ores at the beginning of the process and, after chromite oxidation, chromate dusts are emitted.

The mono- and di-chromates serve as pigments, as corrosion-inhibitors, as oxidizing agents in dyeing, tanning and synthesis of organic and inorganic chemicals.

The chrome plating industry accounts for the largest quantities of chromium trioxide as chromic acid, which can be emitted as a mist during evolution of hydrogen bubbles.

Chromates and chromic oxide, combined with zinc, lead, iron, barium, molybdenum, and strontium to form a variety of colors, serve as pigments. Primer paints and dips containing chromates are used in the construction steel and automobile industries.

Dichromates are used in printing and reproducing processes and serve as mordants in the textile industry.

Chromium carbonyl serves as a catalyst for olefin polymerization and as a gasoline additive.

Chromium chemicals, mostly as chromates, are used in manufacturing fungicides and as wood preservatives (industrial cooling towers). Other manufacturing uses include production of paper matches ($K_2Cr_2O_7$), fireworks, dry-cell batteries (lithium chromate), and antistatic additives for fuels (chromium salt of alkylated salicylic acid).

Other emission sources are industries processing asbestos, manufacturing cements, and burning coal. Chromium emissions from coal-fired power plants have been reported as 18-500 $\mu g/m^3$ after emission controls.

Chromium melts at 1890°C and boils at 2480°C. The trioxide melts and begins to decompose at 197°C with loss of oxygen to form lower oxides. The melting and boiling points of chromic oxide are 1990°C and ∿3000°C, respectively.

The volatilization of chromic oxide can be enhanced by forming chromium trioxide in an oxygen atmosphere. Further enhancement of volatilization occurs with presence of water in the oxygen atmosphere and in a dynamic system with a considerable flow of gas (ref. 5). Chromium trioxide has been observed on the surface of chromic oxide at relatively low process temperatures, 100-300°C (ref. 6). These data suggest the possibility that under certain conditions difficulties may be encountered in attempting to collect quantitatively small quantities of oxides of chromium by using physical filtering methods and high volume flow rates for excessively long sampling periods.

Other chromium compounds and some selected physical constants are: chromium carbonyl - sublimes at room temperature, sinters at 90°C, decomposes at 130°C, and explodes at 210°C; chromic chloride - sublimes at 1300°C; chromic fluoride - b.p. >1100°C; chromic formate - decomposes above 300°C; chromic nitrate - decomposes above 60°C; chromous fluoride - b.p. >1300°C; chromyl chloride - b.p. 117°C; chromyl fluoride - sublimes at 2916°C; lead chromate - m.p. 844°C; potassium chromate - m.p. 975°C; potassium dichromate - m.p. 398°C, decomposes ∿500°C; sodium chromate - m.p. 20°C; sodium dichromate - m.p. 356.7°C; ammonium dichromate - decomposes ∿180°C, ignites readily.

The Threshold Limit Values (A.C.G.I.H. 1967-TLV) for chromium and its compounds are: chromium - 1 mg/m^3; chromates - 0.1 mg/m^3; chromic salts, soluble - 0.5 mg/m^3; chromous salts, soluble - 0.5 mg/m^3; chromium, insoluble compounds - 1 mg/m^3; chromium trioxide - 0.1 mg/m^3.

2.4 Copper and Its Compounds

The ores of copper are categorized as: (1) native ores (pure metal), (2) oxide ores, and (3) sulfide ores. At the present time, only a very small proportion of U. S. copper comes from native ore. The original deposits of oxide ores are largely depleted. Currently, the sulfide ores are the most important sources of copper (ref. 7).

The sulfide ores are usually complex mixtures of copper and iron sulfides associated with compounds of iron, zinc, arsenic, antimony, bismuth, selenium, tellurium, silver, gold and platinum. Most domestic ores contain less than 2% Cu although imported ores contain 20, 30, and even 50% Cu. U. S. ores are generally treated at the mine by a concentration process to upgrade the quality.

The smelting process is generally carried out in a blast furnace or a reverberatory furnace. The flue dust will consist of both original and decomposed, or partially decomposed, particles of ore, flux, furnace lining, and fuel.

Analyses (ref. 8) of flue dust from roasters, reverbatory furnaces, blast furnaces and converters have the following ranges: Cu (5-32%), S (6-14%), SiO_2 (5-26%), FeO (6-35%), CaO (0.3-6.4%), Al_2O_3 (7-8%), Pb(6-20%), with smaller amounts of Ag and Au.

A large percentage of the copper is used as alloys - brasses, tin bronzes, aluminum bronzes, nickel silvers, and the cupronickels. Addition of magnesium, beryllium, aluminum and silicon have been used to retard oxidation of copper. Other elements (Sn, Ag, Mn, P, Cd, Sb, S, As, Ni, Au, Si, Zn, and Bi) change the softening temperature. Other elements - Fe, Te, Se, Co, Pb, Cr - can also be present in the alloys.

Cupric acetate (b.p. 240°C) is a basic raw material for insecticides (arsenite); basic cupric acetate is important as catalytic ingredient in organic synthesis. Basic cupric carbonate serves as a raw material, a pigment (ceramics, paint and varnish industries), a fungicide, and a pickling agent for brass.

Cuprous chloride (b.p. 1366°C) is used as a catalyst in organic and inorganic chemicals manufacture and as a condensing agent for soaps, fats, and oils. It is used in the petroleum industry as a decolorizing and desulfurizing agent. It is also used in denitration of nitrocellulose. Cupric chloride [b.p. 993°C (dec.)] serves as a mordant in textile industry; it is used in refining of copper, gold, and silver, in photography and in deodorization and desulfurization of petroleum distillates. Cupric oxychlorides are formed by exposure of cupric chloride to air and are used as pigments and fungicides.

Cuprous bromide has a boiling point of 1345°C; the cupric bromide (m.p. 498°C) is used in photography and organic synthesis. Cuprous iodide boils at 1290°C. Cuprous fluoride sublimes at 1100°C.

Cupric nitrate, as tri- and hexa-hydrates, boils with decomposition and loss of nitric acid at 170°C and is used in electroplating solutions.

The most important oxides are cuprous and cupric forms. Cuprous oxide boils with loss of oxygen at 1800°C and is manufactured by furnace or electrolytic methods. It is also produced as a by-product of the metallurgy of copper refining and fabrication. Cuprous oxide is used in production of copper salts, in ceramics, in porcelain glaze, in electroplating, in paint, as a fungicide, and as a rectifier in the electrochemical industry. Cupric oxide decomposes at 1026°C; reduction to copper occurs when heated in H_2, CO and many carbon compounds. Cupric oxide is used extensively for preparing cuprammonium hydroxide solution in rayon industry and as a pigment in glasses, glazes, and enamels. It is also used in the petroleum industry for desulfurizing oils.

Cupric hydroxide serves as a mordant and pigment.

Cupric sulfate pentahydrate is the most important of copper chemicals. It decomposes to cupric oxide at 650°C and effloresces in dry air, giving off two molecules of water.

Copper sulfate is the starting material for the preparation of many copper compounds, but has its greatest use as a fungicide. It is also used as a "sweetening" agent in oil refining and as an algaecide. Other uses include preparation of copper ferrocyanide, diazo colors, as a mordant, and as an electrolyte.

Cuprous and cupric sulfides are important sources of copper. Cuprous sulfide decomposes to cupric sulfide, cupric sulfate, and sulfur dioxide when heated in air, but in absence of air only copper and cupric sulfide are formed. At red heat, hydrogen slowly and completely reduces cuprous sulfide, but carbon and carbon monoxide have no appreciable action. Exposure to chlorine results in slow decomposition, and slight decomposition occurs with presence of CO_2.

Cupric sulfide boils with decomposition at 2200°C. When dry, cupric sulfide is stable in air, but when moist it oxidizes to cupric sulfate on exposure to air. In absence of air, cupric sulfide decomposes to cuprous sulfide and sulfur when heated to redness. Reduction takes place in the presence of hydrogen.

The Threshold Limit Values (A.C.G.I.H. - 1967) reported for copper-dusts and mists, and for copper-fume are 1.0 mg/m^3 and 0.1 mg/m^3, respectively.

2.5 Manganese and Its Compounds

In a literature review of manganese and its compounds, Sullivan (ref. 9) identifies the major emission sources. The major emissions of manganese compounds occur in the iron and steel industry - ferromanganese blast furnaces, electric-arc furnaces, and basic oxygen and open-hearth furnaces. Sullivan (ref. 9) reports that the particulates from a ferromanganese furnace are extremely small (0.1 to 1 micron) and contain manganese (15-25%), iron (0.3-0.5%), sodium and potassium oxides (8-15%), silica (9-19%), alumina (3-11%), calcium oxide (8-15%), magnesium oxide (4-6%), sulfur (5-7%) and carbon (1-2%). Somewhat similar data (ref. 9) are reported for electric-arc furnaces where dust and fume particulate contain approximately 4% MnO with 70% of the particles less than 5µ in diameter.

Power plants and steam generator systems burning fossil fuels - coal and residual fuel oils - emit particulate containing approximately 60-400 $\mu g/m^3$ when coal-fired and approximately 25 $\mu g/m^3$ when fired with residual fuel oils (ref. 9).

Most manganese emissions from these sources are in the form of oxides - MnO, MnO_2, Mn_2O_3, and Mn_3O_4. Manganese and MnO when heated in air are readily converted to Mn_2O_3 and Mn_3O_4, respectively; MnO_2 (307-600°C) and Mn_2O_3 (800-1200°C) lose oxygen to form Mn_2O_3 and Mn_3O_4, respectively, when heated. However, in the presence of SO_2 and NO_2, these oxides, particularly MnO_2, react to produce sulfates, dithionates, and nitrates.

Manganese is combined with many elements in the common manganese ores. These impurities can be classified into four general groups: (1) metal - iron, zinc, lead, copper, and silver;
(2) gangue - silica, alumina, lime, magnesia, and baria;
(3) volatile matter - water, carbon dioxide, organic matter;
(4) nonmetallics - sulfur and phosphorus (ref. 10).

Manganese is used in iron, aluminum, aluminum bronze, constantan, manganese bronze, Monel, nickel-chromium, nickel-silver, and copper alloys. A large number of manganese compounds are produced commercially, but the major products are the permanganates, manganese carbonyls, manganese dioxide, manganous acetate, manganese chloride, manganous sulfates and manganese soaps.

The permanganates are used commercially as oxidizing agents. Manganese carbonyls, e.g., methylcyclopentadienyl manganese tricarbonyl, serve as antiknock and smoke inhibiting fuel additives. Many uses exist for manganese dioxide, but major application is in production of dry cell batteries. Manganous acetate is a mordant in dyeing, tanning and finishing leather, a component of fertilizers, a drier in paint and varnish, and a catalyst. Manganese chloride is a chemical intermediate; manganous sulfate is used also as a chemical intermediate and in fertilizers or crop sprays. Manganese soaps are driers, lubricants (wire drawing), and catalysts.

Other sources of manganese emissions include the fertilizer industry - manganous acetate, manganous sulfate, and manganese ethylene—bis-dithiocarbamate; control of sulfur dioxide, mercaptan, and sulfide emissions; and welding shops.

Manganese boils at 1900°C and manganese dichloride has a boiling point of 1190°C. Most other halides decompose when heated. Manganous sulfate decomposes at ∿850°C, and the dioxide (307-600°C) and sesqui-oxide (800-1200°C) lose oxygen when heated.

Manganese organometallic compounds are very volatile. Typical boiling points are: 164-8°C @ 10 mm (di-tert-butylcyclopentadienyl manganese tricarbonyl) and 150°C @ 28-29 mm (tert-butylcyclopentadienyl manganese tricarbonyl).

The Threshold Limit Values (A.C.G.I.H - 1967) for manganese are reported as a ceiling "C" limit value of 5 mg/m^3. The U.S.S.R.

has recommended a 24-hour limit of 10 μg/m³ and a maximum allowable one-time concentration of 30 μg/m³ for manganese and its compounds (ref. 9).

2.6 Nickel and Its Compounds

Nickel or its compounds is emitted from metallurgical plants using nickel, nickel plating facilities, production facilities preparing nickel compounds, power plants and steam generating systems burning coal and oil; and incinerators (ref. 11).

The most common nickel minerals are sulfides and oxides; others having less importance are silicates and arsenicals. The silicate ore, garnierite, is refined in the United States in electric furnaces to yield ferronickel. Most nickel is imported after being refined.

The principal use of nickel is in the metallurgical industry for preparing alloys, e.g., stainless steels and specialty alloys containing high nickel contents. Other uses include nickel plating - electroplating, chemical plating, electroforming, nickel cladding, spraying and fusing of powdered nickel, and chemical vapor deposition by decomposition of nickel carbonyl, nickel chloride, or nickel acetylacetonate.

Nickel and nickel carbonyl serve as catalysts. Thermal decomposition of nickel carbonyl is used to produce high purity, finely powdered nickel for powder metallurgy. Nickel carbonyl, cyclopentadienyl nickel complexes, nickel alkylphosphates, and nickel chelates of salicylaldehyde nitrites and β-diketones are used as fuel additives. Nickel carbonyl can be formed at 25°C by reaction of carbon monoxide and powdered nickel or nickel pipe.

Nickel acetate serves as a mordant and catalyst; nickel carbonate (basic) and nickel formate are intermediates in preparing finely divided nickel catalysts. Nickel chloride is used in electroplating and as an intermediate for preparation of nickel catalysts.

Nickel nitrate serves primarily as an intermediate for preparing nickel catalysts, particularly impregnated nickel catalysts.

Nickel monoxide is the most common oxide and is generally prepared by calcining sulfide ores although hydroxide, carbonate, formate, nitrate and other salts are also used. A green nickel oxide, containing 76.0% nickel, a fraction of a percent of cobalt, 0.5% iron, 0.25% copper, and 0.75% sulfur, is formed from nickel sulfide. The green form is only partially soluble in acids. An additional calcining step with sodium carbonate yields a black modification with lower sulfur (∿0.03%) and higher solubility. Nickel oxide is used in production of ferrous and nonferrous alloys, as an ingredient in enamel frits, as a pigment in glazes, as a coloring and decoloring agent in glass manufacture, as a raw material for preparing ferrites, and as a reagent for other nickel compounds and catalysts.

Nickel hydroxide is usually prepared from nickel sulfate and sodium hydroxide. The hydroxide is used in electroplating, in alkaline storage batteries, and in preparing nickel catalysts and salts of organic acids.

Nickel sulfate, as the hexahydrate, is the major nickel salt of commerce and is prepared from high-sulfur nickel shot and hot concentrated sulfuric acid. The sulfate is the most widely used nickel compound. It is an important constituent of nickel-plating baths, is an intermediate for preparing nickel catalysts, and is a reagent for preparing other nickel compounds.

Nickel ammonium sulfate hexahydrate is a double salt of nickel sulfate with ammonium sulfate and is useful in nickel-plating baths.

Nickel sulfide can exist in several forms having varying degrees of solubility depending on the method of preparation.

The three most common nickel soaps are the naphthenate, oleate and stearate. They have been used as special lubricants in metal drawing, and as crankcase lubricants.

Nickel ferrites belong to a class of mixed oxides of the type $MO \cdot Fe_2O_3$ where M is one or more divalent metals as Mg, Zn, Ni, Co, Fe, and Mn. These materials require substantial quantities of nickel oxide and are formed by high temperature sintering of mixtures of oxides under strongly oxidizing conditions. They possess useful magnetic properties and are used in the electronics industry.

Nickel forms a number of complexes with ammonia, amines, diamines, dialkyldithiocarbamates, and oximes. Nickel amines are used in extracting nickel from oxidized ores; carbamates serve as antioxidants, fungicides, and inhibitors to prevent cracking in GR-S rubber; oximes can be used as pigments.

The boiling points of nickel, nickel carbonyl, and nickel chloride are 2900°C, 43°C, and 973°C, respectively. Nickel sulfate decomposes above 840°C, evolving SO_3 and yielding a residue of nickel oxide. Nickel sulfide melts at 797°C and yields a basic sulfate on heating in air. The nickel nitrate of commerce is usually the hexahydrate that melts or dissolves in its own water of crystallization at about 55°C and with additional heating loses water up to 105°C, at which temperature water vapor and nitrous oxide fumes are evolved to yield a residue of NiO. At about 200°C, nickel formate starts to decompose, yielding nickel, carbon dioxide, hydrogen, water, carbon monoxide, and a trace of methane.

Nickel chloride exists more commonly as the hexahydrate which loses water on heating to form lower hydrates and finally is completely dehydrated by gentle heating above 140°C. The anhydrous salt is sublimed by further heating in vacuo or in a stream of hydrogen chloride. The vapor pressure of the anhydrous salt is 38.9 mm @ 541°C. When sublimation occurs in air, some decomposition occurs, forming chlorine and nickel oxide.

Nickel is also emitted in facilities handling asbestos material. Chrysolite contains from approximately 0.1-0.2% nickel. Nickel emissions as fly ash from coal-fired power plants after abatement controls are reported as ranging from 130-690 μg/scf (ref. 12). Fly ash from residual fuel oil has been reported as containing 1.8 to 13.2% nickel oxide (ref. 13).

The Threshold Limit Values (A.C.G.I.H. - 1967) are 1 mg/m^3 for nickel-metal and solid compounds and 0.007 mg/m^3 for nickel carbonyl.

2.7 Vanadium and Its Compounds

Industrial stack emissions of vanadium occur from industries producing the metal, its chemical compounds and alloys. In addition, considerable amounts are emitted by power plants and utilities burning coal and residual or crude oils. Data on emission sources and types of emissions have been reported by Athanassiadis (ref. 14). Because of the affinity of vanadium for oxygen, carbon, and nitrogen, it is difficult to produce the elemental metal.

The most important ores are the sulfides or partially oxidized sulfides, the vanadates, the carnotite-roscollite minerals - $K_2O \cdot 2VO_3 \cdot V_2O_5 \cdot 3H_2O$ and $K(V,Al_2)(AlSi_3)O_{10}(OH,F)_2$, the lead-zinc-copper-vanadates, the chlorovanadates, the titaniferrous magnetites, phosphate rock, chromite ore, and ferrophosphorus ores.

Vanadium is recovered from ores by ion exchange and solvent extraction, by acid precipitation, and by a leach roasting process. The product of the processing of the ores is a sodium and/or calcium hexavanadate and is usually expressed as vanadium pentoxide.

A highly dispersed aerosol of vanadium pentoxide is formed from condensing vapor during the smelting operation. Prior to use in alloying, the pentoxide is reduced in a slow process to lower oxides and finally metal. At the temperatures (above 3000°C) of the alloying processes, considerable amounts of volatile pentoxide (b.p. 1750°C w/decomposition) can be generated. Melting of ferrovanadium results in pentoxide concentrations in working environments of 68,000 $\mu g/m^3$ of air, and concentrations of lower oxides up to 450 $\mu g/m^3$ of air (ref. 14).

Reduction of the oxide is generally accomplished with carbon, with silicon, or with aluminum. The major alloys are ferrovanadium, vanadium-carbide, vanadium-silicon, and vanadium-aluminum.

A large variety of vanadium compounds with vanadium in various valence states can be formed. In general, the halides are hygroscopic and hydrolyze in water. Both the halides and oxyhalides are volatile - VCl_4 (b.p. 148.5°C); VF_3 (sublimes at red heat), VOCl (b.p. 127°C); $VOCl_3$ (b.p. 126.7°C); VOF_3 (b.p. 480°C); VF_5 (b.p. 47.9°C). Several oxides exist; V_2O_5 is sold commercially and is formed when the vanadium oxides, chlorides or oxychlorides are heated in air. V_2O_5 dissociates into VO_2 and oxygen at temperatures only slightly above its melting point (690°C). Numerous vanadates can be formed. Also, a variety of sulfates have been prepared.

Because the chemical and physical characteristics of the vanadium compounds differ widely, many uses exist. In catalysis, many different vanadium compounds have been used. Two of the more important compounds are V_2O_5 (particularly in the contact process for sulfuric acid) and $VOCl_3$ in ethylene-propylene synthetic rubbers.

Other uses include medicinals (antiseptic and inhibitor of micro-organism growth); dye manufacture (aniline black); inks (indelible inks and quick-drying inks promoted by ammonium metavanadate); glass making (actinic glasses); ceramics; photography; metal soaps (driers).

Power plants and utilities using fossil fuels - residual and crude oils, and coals - and petroleum refineries of crude, which burn crude oil or residuals, emit vanadium compounds as inorganic particulate and possibly as organo-complexes. The concentration of vanadium from fly ash collected from coal-fired power plants after the abatement controls was reported as 230-390 $\mu g/m^3$ and 1,350-1,580 $\mu g/m^3$ (ref. 12).

The Threshold Limit Values (A.C.G.I.H. - 1967) for vanadium (V_2O_5) dust and vanadium (V_2O_5) fume are 0.5 mg/m^3 and 0.1 mg/m^3, where the value for dust is a ceiling "C" limit that should not be exceeded and the value for fume is a time-weighted average concentration for an 8-hour working day.

3. CANDIDATE ANALYTICAL TECHNIQUES

Except for special cases, e.g., nickel carbonyl, boranes, and chromic acid mist, no direct reading instruments for field and continuous or semi-continuous application are available for measuring Ba, B, Cr, Cu, Mn, Ni, and V in ambient air or in stack emissions.

Laboratory methods are based on collecting dust or fumes with filter paper samplers, electrostatic precipitators, and/or impingers.

Analytical techniques relying on instrumental methods have been applied to measure Ba, B, Cr, Cu, Mn, Ni, and V in various media, including particulate collected from ambient air. The techniques used predominantly are colorimetry, atomic absorption spectrophotometry, atomic fluorescence, emission spectroscopy, x-ray fluorescence, neutron activation analysis and mass spectrometry. Most of these methods are based on analyses of particulate only when collected on filters (paper, organic membrane or glass fiber) and suffer from the possibility of potential loss by vaporizing volatile compounds from stack emissions when large volumes of air are drawn over the collected particulate. This effect would be noticed readily when collecting compounds that are obviously volatile, but the effect could occur also in special cases, e.g., the volatilization of chromic oxide can be enhanced by forming chromium trioxide in an oxygen atmosphere, particularly in a dynamic system with a considerable flow of gas. Some of this loss can be minimized by a tandem arrangement of filter and impinger containing a collecting liquid. The vaporization losses on filters could be moderately high when sampling heated stack gases.

No attempt is made in this report to cover the numerous spectrophotometric or wet chemical methods that have been applied to the determination of the subject elements. Information that is pertinent to technology related to the continuous or short-term intermittent monitoring of the seven metals is reported. No analytical technique is currently available that can be immediately and directly applied to the analysis of total B, Ba, Cr, Cu, Mn, Ni, and V, as vapor, fume, and particulate.

The following sections contain technology related to analytical methods that can be applied to the continuous or short term measurement of metals from stack emissions. Although a variety of techniques are presented, the most attractive methods for general application (vapor and particulate) based on selectivity and sensitivity, are absorption and emission spectroscopy. Others, e.g., x-ray fluorescence, may find application in measuring particulate and some, e.g., gas chromatography, would provide specific analyses for nickel carbonyl and organo-metallics.

3.1 Atomic Absorption Spectrophotometry

Because of moderately high sensitivity and good specificity, atomic absorption spectrophotometry has been used to measure trace quantities of metallic elements collected from ambient air after dissolution of the particulate in acid. The major problem in applying the technique to continuous monitoring of stack emissions for B, Ba, Cr, Cu, Mn, Ni, and V is the inability to handle refractory compounds, for example, B, and elements that readily form stable compounds - VO - in the flame. Serious interelement and matrix effects are observed.

All seven elements are affected by matrix effects and compound formation, particularly in air- or oxygen-acetylene flames. As a consequence, direct aspiration of air-contaminated gas into the flame has not been used to any large degree for continuous monitoring of metallic elements in air or stack emissions.

Depending on the concentrations of the element in the stack and the matrix, a continuous monitoring system based on direct aspiration of stack gas or air into the acetylene fueled flame can be developed, but the estimated detection limit would probably not be <1 mg/m^3 without a preconcentration step.

The direct aspiration of nickel concentrated into a small volume air stream is reported but no specific details are given. The apparatus (Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer) modified for simultaneous determination of four selected elements was described by Zweibaum and Moorhead (ref. 15). The system was designed for continuous monitoring of several elements concentrated from the atmosphere into a small volume air stream. The air stream with enriched sample content is fed directly and continuously into the burner nebulizer. Applications to nickel are reported, but no data are given.

The highest sensitivity and minimal matrix and chemical interferences for B, Ba, Cr, Cu, Mn, Ni and V are attained with nitrous oxide as the oxidant and with a nitrogen sheath gas to restrict interaction of ambient air with the chemical species of the flame.

Interelement effects can also be eliminated by using a high energy plasma to atomize the elements being measured. The major problem in applying this technique is maintaining high levels of ground state atoms, but low ionization efficiencies, in the plasma. Energy from the plasma may ionize the element sought, thus reducing the population of ground state atoms which must be high to attain high sensitivities for the atomic absorption phenomenon.

Improved atomic absorption spectrophotometric detection limits (<1 ppm) for boron in aqueous solutions have been attained by using the Kranz d.c. plasmajet as a source of atomic vapors (ref. 16). No interelement effects were found with 50 ppm of Al, Ba, Fe, Li, K, Mn, and Zn, and no difference in the absorption signal was found in the presence of Cl^-, $SO_4^=$, or NO_3^- ions.

The Kranz d.c. plasmajet is a gas stabilized d.c. arc burning between thoriated tungsten electrodes. Nitrogen was used as the carrier gas during the boron analysis.

The technique developed by Loften, et al. (ref. 17) to monitor Pb as alkyllead compound should be considered as an approach to continuous monitoring of other metal elements. The method is based on the reduction of lead in air by carbon monoxide formed from oxygen in the air specimen as it passes through a hot bed of carbon. Elemental lead produced in this manner is introduced into the long optical path of a nonflame atomic absorption spectrophotometer. With other elements, data on efficiencies of the reducing reaction and on the capability to maintain the elemental ground state atoms in the vapor state must be obtained.

Other possibilities include using a high-frequency (5 MHz) induction plasma in a reducing mode (ref. 18, 19). Little data are available but high sensitivities are attainable for elements in powdered samples which were introduced directly.

Conventional atomic absorption spectrophotometry uses a monochromator system to isolate the characteristic radiation. However, increased stability of the atomic absorption spectrophotometric analyses for Ni can be attained by using a resonance lamp as a monochromator (ref. 20). The wavelength setting is stable under the most rigorous conditions and, with provision for automatic setting of full-scale deflection, the system requires little, if any, adjustment. Changes in ambient temperature or pressure, or small mechanical vibrations have no effect. The resonance reemission from Ni vapor provides a means for isolating the resonance lines at 3415, 3515, and 3524 Å; no data are reported for the more sensitive line at 2320 Å. For routine determinations of Ni in the range of 0.05-2%, the accuracy for single determinations was ±5.1% of the mean at the 95% confidence level (ref. 20).

Also, improved sensitivity and good resolution can be obtained by atomic absorption or fluorescence spectrophotometric techniques without monochromators by using selective modulation or resonance detectors for isolating resonance lines and by coupling a solar-blind photomultiplier to the system. The application of solar-blind photomultipliers to measuring nickel has been demonstrated (ref. 21). No specific data are reported.

A continuous measuring technique for nickel carbonyl (specific if no other reducing agents are present) was developed by Vol'berg (ref. 22) based on the atomic absorption phenomenon but using a low cost mercury vapor photometer. The method determines microquantities of nickel carbonyl in air by measuring the amount of mercury liberated by the reaction of the nickel carbonyl with red HgO @ 200°C. The elemental mercury is measured by ultraviolet absorption techniques.

The following summaries on atomic absorption techniques for B, Ba, Cr, Cu, Mn, Ni and V are presented to show the detection limits and potential problems with spectral and chemical interferences.

Atomic absorption spectrometric analyses of acid extracts of particulate collected on glass fiber filters and membrane filters have been used extensively for measuring particulate from ambient air (ref. 23). The sampling times and sample preparation times are long, but relatively low detection limits are attainable.

Care must be taken to prevent loss or contamination of the sample. All reagents must be distilled to remove metal contaminants and all glassware must be carefully cleaned (soaking in 20% nitric acid for 2 to 6 hours).

The solids content must be maintained at <0.5%. Also, silica extracted from glass fiber filters and from the particulate sample must be eliminated from the solutions (settling for 12 to 24 hours followed by centrifugation) or significant interferences with Fe, Ca, Mn, and Zn occur.

Glass fiber filters yield background contamination of elements such as Fe, Ba, Zn and others. Membrane filters must be used to measure these elements.

Based on an integrated 2000 m^3 air sample, the following detection limits were obtained: Ba (0.02 $\mu g/m^3$), Cr (0.002 $\mu g/m^3$), Cu (0.001 $\mu g/m^3$), Mn (0.001 $\mu g/m^3$), Ni (0.004 g/m), and V (0.01 $\mu g/m^3$).

Particulate, collected from ambient air by filtering air through a Millipore membrane for 8 hours, was analyzed for Cr, Ni, Mn, and Cu by an atomic absorption technique (ref. 24). The acetate based membrane is destroyed with acetone and, after evaporating the solvent, the residue is ashed in a muffle furnace at 550°C for one hour. The ash is extracted with hot nitric acid to prepare a solution specimen for atomic absorption analysis.

A lean air-acetylene flame was found satisfactory for the determinations of Cr, Ni, Mn, and Cu, although a reduction in sensitivity was observed with Cr.

Lean-flame conditions gave much less interelement effect in comparison with a fuel-rich flame. However, significant interelement effects are reported with the addition of one of the four elements to the one being measured. Anionic interferences were also noted for $HClO_4$, H_2SO_4, H_3PO_4, HCl, and HNO_3 additions.

Glass fiber filters were found to be contaminated with significant amounts (6-20 μg/filter) of Cr, Ni, Mn, and Cu, plus Ba, Pb, Zn, Fe, Ca, etc., which not only contribute to the level of analyte but also may cause interelement effects. Contamination of 0.1 to 0.5 μg of each of the four elements - Cr, Ni, Mn, and Cu - was found in the organic membrane filters.

To minimize the interelement effects, all analyses were performed by the standard addition method.

Ambient air particulate samples collected on glass fiber filters, ashed with a low temperature asher, and leached with nitric acid have been analyzed by atomic absorption spectrophotometry for vanadium, nickel, chromium, manganese, copper and other elements (ref. 25). The total analytical procedure is time consuming (sampling - 7 days @ 20 ft^3/min; ashing - 2-14 hr; extraction - approx. 3 hrs; atomic absorption measurement - approx. 10 min.). The following detection limits and average precision are reported: V - 0.094 $\mu g/m^3$ (21%); Ni - 0.006 $\mu g/m^3$ (13%); Cr - 0.003 $\mu g/m^3$ (22%); Mn - 0.002 $\mu g/m^3$ (10%); Cu - 0.003 $\mu g/m^3$ (9%).

The determination of Mn in aqueous solutions by atomic absorption spectrophotometry is improved by deaeration of the diluting water (ref. 26). Some compound formation apparently occurs with dissolved oxygen.

Iron interferences in the atomic absorption flame photometric determinations of Co, Cr, Cu, Mn and Ni were studied by Ramirez-Munoz and Roth (ref. 27). With air-acetylene flames, increasing amounts of Fe decreased sensitivity for all elements. Fe interferences were greater with Cr, and less with Mn. The possible formation of Fe-Cr compounds is considered responsible for some signal decrease. (Note - A hotter flame, e.g., N_2O-C_2H_2, may minimize the effect.)

The reaction of a metal oxide species with an overexcited molecule of a C species, e.g. C_2 or CH, in a fuel-rich air-C_2H_2 flame is a possible cause of the decrease observed in the atomic absorption of Fe, Cr, Co, Cu, and Ni in flames having a C_2H_2-air ratio greater than a critical value which is characteristic for each metal. The absorption decrease was observed with SO_4^{2-} and NO_3^- solutions of the metals, but not in Cl^- media (ref. 28).

The determination of barium is best performed with a nitrous oxide-acetylene flame even though the flame temperature is sufficient to cause a relatively high degree of ionization and attendant loss of ground state atoms necessary for the atomic absorption process (ref. 29). The nitrous oxide-acetylene flame minimizes compound formation encountered in other flame systems. However, a problem due to high emissivity of the nitrous oxide-acetylene flame at the analytical wavelength for barium (5536 Å) occurs. The cause is inadequate emission from the hollow cathode lamp (ref. 30).

Boron has been determined by atomic absorption spectrophotometry (2498 Å) with a nitrous oxide-acetylene flame. A detection limit of 6 $\mu g/ml$ has been attained (ref. 31).

When using a graphite tube furnace (P.E. HGA-70) in nonflame atomic absorption spectrophotometry, an intense C_2 emission line 0.2 Å away from the Ba resonance line can cause significant interference.

Marshall and Schrenk (ref. 32) performed detailed evaluation of various flames and matrices for the analysis for vanadium (3185.4 Å) by atomic absorption spectrophotometry. Extensive interference from Al, Bi, Cr, Fe, K, Li, Sb, Ti, Zn, acetate and phosphate were encountered in an oxyacetylene flame. Several explanations are given including formation of nonvolatile vanadates or intermetallic compounds. A detection limit of 15 μg V/ml is reported.

A number of elements interfere with the atomic absorption measurement of V at 3185.4 Å. Chelation techniques and solvent extraction prevent interferences from all elements except Co^{II}, Cu, Se and W^{VI} (ref. 33). The best results are obtained with a nitrous oxide-acetylene flame.

Atomic absorption and flame emission spectroscopic determinations of Ba in aqueous solution were compared by computer techniques (ref. 34). In the absence of interferences, atomic absorption with air-acetylene flame is the preferred method for 10-500 μg Ba/ml. In the presence of interferences or at lower concentrations (1-100 μg/ml), atomic absorption with the $N_2O-C_2H_2$ flame is the most convenient method. For <1.0 μg Ba/ml, flame emission with $N_2O-C_2H_2$ flame is preferred and gives a detection limit of 0.0035 μg Ba/ml, as compared to 0.03 and 0.72 μg Ba/ml for atomic absorption with the $N_2O-C_2H_2$ and air-C_2H_2 flames, respectively.

A large number of elements are known to interfere with conventional flame atomic absorption spectrophotometric analyses for chromium. A summary of these interferences and methods for overcoming them is presented by Hurlbut and Chriswell (ref. 35). The elements (Mg, Ba, Ti, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Cd, Hg, Al, Bi, and Ce) and the compounds (H_3PO_4, H_2SO_4 and NH_4OH) interfere with the absorption by Cr at 3579 Å. The most effective surpressor of interference was Na_2SO_4.

Sachdev, Robinson, and West (ref. 36) developed an atomic absorption technique for measuring Mn and Ni in air particulate collected on filter paper. After ashing, the residue is dissolved in hydrochloric acid and measurements are made with atomic absorption spectrophotometric equipment modified with a quartz T-piece adapter to provide a 15 cm optical path. With the adapter, 10- to 15-fold increase in sensitivities was obtained. Sensitivities of 0.01 mg/l (Mn) and 0.02 mg/l (Ni) for 1% absorption are observed. Interference effects were studied, but only a slight suppression on the absorption of manganese was observed with titanium, vanadium, and zirconium. These interferences were removed by complexing the ions with fluoride.

Some, but not all, cationic interferences in the atomic absorption spectrophotometry of chromium can be eliminated by using a nitrous oxide-acetylene flame (ref. 37). With an air-C_2H_2 flame, the atomic absorption of Cr (357.9 nm), as Cr(III) and Cr(VI) solutions, was enhanced by Cu > Ba > Al > Mg $\geq$ Ca while Na, K, Sr, Zn and Sn depressed the Cr absorption. Fe depressed the absorption of Cr(III), but enhanced that of Cr(VI); Mn and Ni depressed Cr(III) absorption, but gave no marked enhancement for Cr(VI). By using the N_2O-C_2H_2 flame, Na, K, Zn, and Fe interferences were eliminated.

3.2 Atomic Fluorescence Spectrophotometry

Better sensitivities for some, but not all, elements are reported for atomic fluorescence techniques when compared to atomic absorption spectrophotometric analyses of the same elements. The technique is not applicable to determinations of all metal elements and has limited value to special cases.

Because of the interatomic quenching effect of fluorescence by nitrogen, direct introduction of air or stack gas emission into the flame is not practical.

The following selected summaries show the effects of instrumental parameters in the application of trace metals in aqueous media and show the development of a simultaneous multielement analyzer.

A detailed study of atomic fluorescence spectrophotometry was performed as applied to the determinations of iron, cobalt, and nickel (ref. 38). The effects of source parameters, optical arrangement, uptake of sample solution, solvent, inorganic acids and 13 other elements were investigated. For aqueous solutions, a detection limit of 0.003 ppm Ni was reported; by using an extraction technique 0.0001 ppm Ni can be detected.

An instrument was designed for simultaneous multi-element analysis using sequentially excited atomic fluorescence radiation. The instrument was used for the simultaneous determination of Ag, Cu, Fe and Mg in aqueous solutions and provided detection limits of 0.002 ppm (Ag), 0.003 ppm (Cu), 0.1 ppm (Fe), and 0.001 ppm (Mg) (ref. 39).

3.3 Emission Spectroscopy

Although emission spectroscopic techniques have been used extensively to measure the metal content of particulate collected by the National Air Sampling Network (ref. 40,41), no data are available for continuous, flow-through, emission spectroscopic studies on airborne or stack emissions of B, Ba, Cr, Cu, Mn, Ni, and V. However, modification of techniques reviewed in other documents in this series, (a) Beryllium and Cadmium, (b) Mercury, and (c) Lead, and reported elsewhere (ref. 42,43,44,45,46) should be considered.

The major limitations of emission spectroscopic techniques are the chemical interferences - compound formation in the excitation zone - and spectral interferences. Compound formation can be minimized by using a sufficiently energetic source, e.g., radio-frequency— or microwave—induced plasma. Spectral interferences can be eliminated by selection of proper analytical lines and by using a monochromator which provides sufficient resolution.

Data relating to flame-, arc- or spark-excitation of optical emission for B, Ba, Cr, Cu, Mn, Ni, and V are reported in the following sections to aid in understanding potential interferences and problems that can be encountered.

Flame photometric analyses of boron in aqueous solutions have been performed based on extraction into an organic solvent and measurement of emission at 546 nm in an oxygen-hydrogen flame (ref. 47). Extraction was complete for <0.4 mg B and 96% B was recovered from solutions containing 0.4-1.0 mg B. Presence of Mn, Ti, Mo, and W caused spectral interference. Fluoride in the aqueous solution reacted with B to give BF_4^- which was not extractable.

Ba has been measured with emission flame photometry (553.6 nm) in a propane-butane-air flame. Interferences from Ca, Cu, Cd, Sr, and Mg are reported (ref. 48).

A number of analytical methods for measuring barium in silicates were evaluated with regard to speed, reliability, and systematic errors (ref. 49). These methods included isotope dilution mass spectrometry, flame emission and absorption spectrometry, x-ray fluorescence spectrography, neutron activation analysis, and classical gravimetric methods. Emission spectrometry, with a spark-solution technique and automated equipment produced rapid and accurate results. Other techniques are reported as not satisfactory as practical routine methods for barium in silicate rocks. In most cases, the other techniques were subject to interference and lengthy separations were required (ref. 49). Routine determination of barium by direct dilution x-ray methods is satisfactory if adequate standards are available and if precautions are observed (ref. 49).

By using a nitrous oxide-acetylene flame, Fassel, et al. (ref. 50) report the "interference-free" determinations of Cr, Cu, Mn, Ni, and V in solutions of low and high alloy steels. Lowest determinable concentrations of 0.002% (Cr), 0.01% (Cu), 0.02% (Mn), 0.005% (Ni), and 0.01% (V) are reported.

A multichannel flame emission spectrometer (ref. 51,52,53) was developed for the simultaneous determination of magnesium

(2852 Å), calcium (5227 Å), copper (3242 Å), manganese (4031 Å), and chromium (4254 Å). Detection limits are 1.0 µg/ml or less for each element in aqueous solutions. The repeatability for each element is excellent, the coefficient of variation ranging from 0.5 for Cr to 3.2% for Cu. The accuracy (comparison of mean value determined and the expected value calculated from the dilution of each original, certified sample) varied - Cr (82%), Cu (90-93%), Mn (92-94%).

The emissivity of chromium increases with a corresponding increase in HCl. Mutual interference exists between Ca and Cr; the intensity of the Cr emission is lower in presence of Ca. A concentration of 300 µg K/ml will affect Mn emission intensity. Phosphate ion decreases the intensity of the emission at 4031 Å for Mn. No interference was observed for nitrate and sulfate ions. By incorporating selected additives into the solutions, interferences can be overcome; the most efficient additive proved to be a solvent system of half-saturated 8-hydroxyquinoline and 0.4M perchloric acid in 1M hydrochloric acid (ref. 51,52,53).

By shielding the secondary reaction zone in an air-C_2H_2 flame with a stream of nitrogen flowing parallel to the flame to prevent access to atmospheric oxygen to its base, higher sensitivities and less interference from bonded molecular emissions are observed with flame emission spectrophotometry (ref. 54). The technique permitted measurement of Ba, Cr, Cu, Mn, Ni, and V by flame emission spectroscopy. The detection limit for all but V was improved by a factor of 10, and V, which was previously undetectable, could be detected to 10 ppm.

A critique on interferences by SiO (molecular band spectra) and Fe (2497.82 Å) on the B 2497.73 Å emission line is presented by Moore (ref. 55). With silicate-bearing rocks, interference from Fe (2497.82 Å) was judged to be of no consequence at least to 10% FeO. A correction method for SiO interference was developed based on extrapolating a baseline from a line connecting tops of SiO band peaks on the longer wavelength side of B + SiO @ 2497.73 Å. For concentrations of boron in the range from 1-520 ppm, a coefficient of variation of 17% was obtained.

By using an argon atmosphere instead of air for determining B in a quartz matrix in a d.c. arc discharge, the interference due to SiO band spectra (2414-2925 Å) is eliminated when B 2497.7 Å is used as an analytical line. A detection limit ~0.5 ppm of B in quartz can be determined (ref. 56).

The suitability of measuring B in steel with the B lines 2496.8 Å, 2088.9 Å, 2089.6 Å, 1826.4 Å and 1825.9 Å with various conditions of excitation under argon was determined with instruments of 4.6 or 7 Å per mm dispersion. The 2089.6 Å and 1825.9 Å lines, although subject to considerable interference by Mo and Cu, respectively, are the only suitable ones (ref. 57

Manganese, chromium, and vanadium were detected in atmospheric dust particles with emission spectroscopy by burning the particulate and the filter paper used to collect the specimen, in flat graphite electrodes after adding graphite powder. By carrying out the excitation in a magnetic field, the relative standard deviations were decreased from $\leq15\%$ to $\leq10\%$. The analytical lines and amount of metals determined were: Mn 2593.73 Å (0.01-3 μg); Cr 2761.74 Å (0.2-10 μg); V 3185.40 Å (0.05-10 μg) (ref. 58).

Spectrographic determination of vanadium by using the V triplet (3183.406 Å; 3183.982 Å; 3185.412 Å) is subject to interference from Ti, Fe, CA, Cr, and Ni (ref. 59).

Snelleman, et al. (ref. 60) developed a technique of optical scanning in the derivative mode (2nd derivative) that minimizes the need for a monochromator of high resolving power, and provides for the use of microsamples. The technique permits the measurement of weak line spectra nested in or on a broad band or continuum. Typical examples of interfering bands are the CaOH bands (5430-6220 Å), MgOH bands (3600-4000 Å) and OH bands (2800-4000 Å). The effectiveness of the technique was demonstrated in the measurement of barium (4 μg/ml) @ 5536 Å in the presence of calcium in a Ca:Ba ratio of 1000:1.

An error exists in reference data (most handbooks) on Cu spectra based on Harrison tables. The intense 2392.627 Å line of the Cu arc spectrum was omitted. Instead the line 2592.627 Å is reported, which does not exist in the Cu arc spectrum (ref. 61).

Increased sensitivity over that by arc- or spark-excitation of optical emission and freedom from chemical compound formation is attained by using high energy excitation sources - radio-frequency or microwave discharge (ref. 62,63,64). With a radio frequency discharge, Dickinson and Fassel (ref. 62), were able to detect B, Ba, Cr, Ni, and V in aqueous solution at the concentrations of 0.03 μg/ml, 0.0001 μg/ml, 0.001 μg/ml, 0.006 μg/ml, and 0.006 μg/ml, respectively. No chemical interferences or matrix effects on spectral line emission intensities were observed.

Operation of radio frequency (2.5 kW) or microwave (2 kW) excitation at atmospheric pressure produces a plasma system of sufficiently high sensible heat to vaporize and excite to optical emission even the most refractory elements and compounds. However, microwave excitation (∿100 watts) yields high sensitivities, but relatively low sensible temperatures and, as a consequence, an external system is needed to vaporize most particulate.

Radio-frequency excitation of optical emission provides an attractive approach for continuous monitoring of vapor and particulate emissions of most metal elements and some nonmetallic elements. Sufficient energy is available to vaporize, decompose, and excite to optical emission most stack effluent (gaseous and particulate).

Fundamental studies using a plasma jet generator (A with nozzle-shaped Cu anode and W rod cathode) in emission spectroscopic determination of Ni, Mn, and Cr in aqueous solution show less interelement effects than with an a.c. arc discharge method. However, when a sample is in water, the background due to H_2O can be so large that the detection limit is not always higher than that by a.c. arc excitation (ref. 65). A simultaneous determination of Ni, Mn, and Cr was developed which required no internal standard and had detection limits lower than conventional techniques (ref. 65,66).

By measuring the emission of Cr radiation @ 4254.346 Å, from a helium plasma generated with an RF induction furnace (3 Mc) a detection limit of 10^{-9} g of Cr has been attained (ref. 67). The system uses a graphite crucible as a receptacle for either liquid or solid samples and can be applied to a wide range of elements. With evaporated solution samples, the precision of the measurement (peak height) is 1-4% depending on the element. A precision of 4-10% was attained with powdered samples.

Chromium was measured with a high frequency (40 mHz) induction plasmatron and emission spectroscopy. Analytical lines and detection limits in an argon plasma are: Cr - 3578.69 Å (1 μg/ml); 3886.80 Å (125 μg/ml); 3919.16 Å (60 μg/ml); 4254.33 Å (2 μg/ml) (ref. 68).

SpectraMetrics Inc. (Burlington, Mass.) has a multi-element spectrometer (SpectraSpan) using an argon plasma (10,000°K) based on an electrode system. The spectrometer can be used in an emission or atomic absorption mode. High spectral resolution is obtained with an echelle grating and a series of polychromator/encoding cassettes. By mixing air or stack gas samples with argon, a continuous measurement of up to 10 elements is possible. (Note - A 401 Process spectrometer is available.) High sensitivities are obtained, h[illegible]o specific data on direct monitoring of metal emissions are reported.

3.4 X-ray Emission Spectroscopy

A number of excitation sources ranging from a Van de Graaff generator to the more common x-ray tube (tungsten target) and radio-isotope sources have been used to measure metal elements in airborne particulate collected on filters. Although high sensitivities and attendant low detection limits result with the Van de Graaff system, devices using the latter excitation sources are more practical for field applications. In all cases, the techniques require the collecting of particulate for measurement.

The major problems associated with the technique involve matrix effects - loss or enhancement of the intensity of the analytical line due to interelement interactions - particle size effects, spectral interferences, and weight, size and power factors. With thin films of particulate, many of these problems can be minimized. Spectral interferences have been reduced by the development Si(Li) semiconductor detectors. Instrument portability has been attained with radioisotope excitation sources.

Cares (ref. 69) considered some of the sampling handling problems encountered in measuring airborne metallic dusts and fumes by conventional x-ray spectrometry. Severe interferences can be encountered from contaminants present in the filter media. Ashless and membrane filters are essentially free from contamination except for traces of iron, potassium, and calcium. Glass fiber filters have relatively high iron and zinc contamination, and contain sufficient calcium, potassium, and barium to create severe interference at or near the principal lines of these elements.

Additional spectral interferences (ref. 69) are also observed for systems using tungsten x-ray target material. Tungsten and copper reflections are observed with varying intensity, depending on the age of the tube and surface characteristics of the sample. With the tungsten target x-ray tube, it is difficult to determine low concentrations of Hg, As, or Se.

Intensity reduction or enhancement result from matrix, sample thickness, particle size, and interelement effects (ref. 69). When using analytical x-ray lines of low energies (long wave lengths), considerable counting losses can result by penetration or burial of particles between fibers of some types of filter paper. Counting losses due to burial were highest in Whatman 41 filter paper and lower, but variable, in glass fiber filters. Absorption losses due to sample matrix are also influenced by the wavelength of the analytical line. Net counts for Cd L_β (3.74 Å) are reduced about 40% from values obtained with Cd K_α (0.536 Å) in a matrix containing an equal amount of iron or silver. Also, although the Cd L_β line is more sensitive than the K_α, a critical sample thickness for Cd L_β occurs at approximately 400 $\mu g/cm^2$.

The principal analytical lines (x-ray) of selected metals of industrial hygiene significance are: Cr (K_α - 2.29 Å), Cu (K_α - 1.54 Å), Mn (K_α - 2.10 Å), Ni (K_α - 1.66 Å), and V (K_α - 2.50 Å).

Problems related to background signals from glass fiber filters used to collect airborne particulate were observed by Leroux and Mahmud (ref. 70). Only lead could be measured without interference in particulate collected on glass fiber filters. Ba, Ni, Cu and other lements would all be subject to interfering background signals emitted from the glass fiber filters. Organic membrane filters have considerably less contaminants; data for Mn collected on organic filters are reported. The authors also conclude that the average air pollution samples weighing less than 1.5 mg/cm^2 can be analyzed without matrix correction for all its elements higher than manganese in the Periodic Table.

Hirt, et al. (ref. 71) developed technology for collecting particulate, for performing x-ray emission spectrographic analyses, and for preparing calibration standards to detect and measure quantitatively heavy metal elements in airborne particulate. One to 100 micrograms of Co, Cr, Fe, Pb, Hg, Ni, Pt, V, and Zn were detected and measured. Particulate was collected on glass fiber filters and analyzed with a Norelco x-ray spectrograph equipped with NaCl crystal and a helium flooded sample chamber.

For deposits less than 200 micrograms on a 2.4 cm filter disk, no reabsorption of secondary x-rays and no lack of penetration of the primary x-rays occurred. Calibration curves were derived from standards prepared by evaporating different volumes of solutions of known concentrations onto an aluminum foil or filter disk made nonabsorbent with acrylic resin impregnant.

Disadvantages of the x-ray emission (fluorescence) method are complications due to inter-element effects and difficulty in preparing proper standards.

Mathematical equations which correct for the interference (absorption and enhancement effects) of CrK_α with MnK_β line have been developed (ref. 72).

Numerous theoretical, mathematical, and empirical techniques have been devised to correct for interelement (matrix) effects. However, a number of deviations from the predicted intensities occur. Mitchell and Kellam (ref. 73) reported several unusual matrix effects when determining combinations of 4th-period elements such as Cr, Fe, Co and Ni. Chromium has an absorbing effect on NiK_α and CuK_α among others, whereas iron will severely absorb NiK_α, and less severely absorbs CuK_α.

Opposite and coexistent with the absorption effect is the enhancement of CrK_α by the absorption of the iron radiation and to a lesser degree by the presence of Co, Ni and Cu.

Interrelated effects do occur. The matrix effect of iron or nickel on CrK_α in a light matrix is an enhancement at low levels of iron and nickel, but, as the iron or nickel reaches a critical level, the CrK_α intensity decreases.

Graham and Bray (ref. 74) observed a linear relationship between excited x-ray intensity and element concentration for film thicknesses up to about 0.1 mg/cm^2 and concluded that in this thickness range absorption effects have no observable influence on x-ray intensity. Based on these observations, metal film standards were prepared.

A correction factor scheme was developed to minimize interelement absorption effects for x-ray analyses for vanadium, zirconium, tungsten, iron, titanium, tantalum and niobium (ref. 75).

A general x-ray spectrographic solution method which provided a single calibration system per element for all materials and acid matrices was used with a x-ray Industrial Quantometer (ref. 76).

Data for an automatic x-ray spectrograph, Autrometer, show a standard deviation of 0.03% for Ni in a 10% nickel alloy (ref. 77). Precision was poorer for trace elements because of the statistical lack of counts. Average accuracy for W, Mn, Ni, Cr, Co, Fe, Mo, and V determinations, between 2 and 23% concentration was 0.77% in comparison with wet analyses.

During x-ray fluorescence analyses of trace elements in sea water, Morris (ref. 78) observed several spectral interferences. Conventional x-ray fluorescence equipment - tungsten target x-ray tube, lithium fluoride crystal, 0.16-mm collimator, vacuum sample chamber, and gas-flow proportional counter with pulse height selection - was used. Unresolved first order $K_{\alpha 1}$ and $K_{\alpha 2}$ lines for V, Cr, Mn, Fe, Co, Ni, Cu, and Zn were used after separating and concentrating these elements from sea water.

The intense first-order tungsten $L_{\alpha 1}$ line at 42.99° and $L_{\alpha 2}$ line at 43.44° emitted by the x-ray tube swamped the $K_{\alpha 1,2}$ emission of 5 ppm amounts of copper and nickel at 44.99° and 48.64°, respectively. These interferences could be corrected by using a titanium filter, but some reduction of the analytical line intensity also occurs. The x-ray fluorescent determination of the transition elements in presence of one another is complicated by the proximity of the first order $K_{\beta 1}$ emissions to the first order K_{α} lines of the next element in order of increasing atomic number. The analytical system could not resolve the $K_{\beta 1}$ line of vanadium at 69.12° from the K_{α} lines of chromium at 69.29° and 69.43°. In addition, the $K_{\beta 1}$ lines of chromium and manganese are only partially resolved from the K_{α} lines of manganese and iron, respectively. The $K_{\beta 1}$ emission of Fe may interfere with the $K_{\alpha 1,2}$ emission of cobalt.

Spectral interferences were minimized by using calibration curves adjusted for each elemental interference. Detection limits of 0.4 µg or better are claimed for 600 sec. counting times.

Boron cannot be measured by conventional x-ray emission techniques. However, by using proton excitation, Kamada et al. (ref. 79) were able to detect down to 0.0014% B in nickel base alloy. A 200 kV proton source and a flat crystal (lead stearate) were used. Considerable background interferences due to low-angle specular reflection from the lead stearate and due to emission lines of base material were observed.

Because of low energy, ultrasoft boron x-rays are easily absorbed in x-ray analytical systems and, unless special analyzer crystals are used, the ultrasoft radiation cannot be resolved.

Film analyzers were prepared from Ba and Pb salts of stearic, behenic, and lignoceric acids, which resolved B K_α lines and allowed the microanalysis of B with high sensitivity (ref. 80). (Note - No specific data are reported.)

An improved method for the determination of barium was developed based on using chromium x-ray tube, rather than tungsten, and $BaL_{\alpha1}$, rather than $BaK_{\alpha1}$ (ref. 81). The major problem with using W x-radiation and the $BaK_{\alpha1}$ analytical line is the low peak-to-background ratio resulting in large part from scattered tungsten radiation. By using chromium radiation and the $BaL_{\alpha1}$ line, the net intensity is approximately three times larger. A detection limit of 0.002% Ba was achieved.

In geologic samples, a detection limit of 10 ppm for barium was attained if corrections for a titanium spectral interference can be made (ref. 82). The first-order titanium $K_{\alpha1}$ line (2.7432 Å) interferes with the barium first-order $L_{\alpha1}$ analytical line (2.7696 Å). Note - The barium $L_{\beta1}$ line, which has the same intensity as the $L_{\alpha1}$ line and no titanium interference, can be used if cerium is absent. $CeL_{\alpha1}$ is a spectral interference for $BaL_{\beta1}$.

Gunn (ref. 83) and Willis, et al. (ref. 84) compared several alternative methods for determing Ba by x-ray fluorescence techniques. The measurements can be performed by using BaK_α or L x-ray lines. To excite BaK_α emission, a higher primary x-ray beam energy is necessary than is available on most spectrometers. Alternatively, the much weaker BaL lines can be used with a Cr primary radiation.

Of the available L lines of Ba the $L_{\alpha1}$ is overlapped by the TiK_α line. The $L_{\beta1}$ line is overlapped by CeL_α line; $L_{\beta2}$ is free of interference, but is very weak. The $L_{\gamma1}$ line is stronger when using a Cr primary tube at 1800 watts; however, the background is strongly curved requiring a curvature correction.

By using 100 KV to 150 KV excitation of W K_α line in the primary tube, analyses based on the BaK_α line can be performed. The standard LiF monochromator crystal is not adequate to diffract the BaK_α line; however, sufficient resolution is obtained with LiF crystal cut to the 220 reflection planes. Using this crystal, the BaK_α line may be resolved from the iodine absorption edge. The iodine interference would occur if a NaI scintillation detector is used. Gunn (ref. 83) reports that, by using the BaK_α lines rather than L lines, considerable improvement is obtained. Total analysis time per determination using BaK_α line is three minutes with a replication error of less than 2%.

The high energy of the BaK_α radiation results in greater penetration of samples than normally encountered with other elements. As a consequence, the analyst must be aware of a potential problem with sample thickness. Excellent replication was found in samples less than infinitely thick for the radiation being used.

Rhodes (ref. 85,86) reviewed the development of x-ray excitation with radioisotope sources and nondispersive energy detection. The relationships of interferences arising from absorption, enhancement, and particle size effects were also discussed. The application of radioisotope sources provides portability and less background scatter of target radiation which is characteristic of the conventional x-ray tube excitation techniques.

A review of energy dispersion techniques, methods of calculation, and interpretation of data from inhomogeneous samples was prepared by Birks (ref. 87).

Rhodes, et al. (ref. 88,89) applied x-ray fluorescence analysis using radioisotope sources for excitation, a Si(Li) detector for energy dispersive spectrometry, and a minicomputer for data reduction and automatic instrument control to determining "heavy element" constituents of airborne particulate collected on filter paper. The technique was used to measure 17 elements including V, Cr, Mn, Ni, and Cu. Based on collecting particulate from an average air volume of 1880 m^3 over 24-hour periods, the following detection limits were attained: V - 0.007 $\mu g/m^3$, Cr - 0.053 $\mu g/m^3$, Mn - 0.027 $\mu g/m^3$, Ni - 0.013 $\mu g/m^3$, and Cu - 0.011 $\mu g/m^3$.

Matrix effects - absorption or enhancement by other elements in the sample - are reduced or eliminated by using thin specimens, $\sim$370 $\mu g/cm^2$. Also, by using thin specimens, the ratio of fluorescent intensity for a given element to the intensity of backscattered (background) radiation is much larger than for infinitely thick specimens.

To obtain the best excitation efficiencies, each sample was irradiated with each of three annular radioisotope source assemblies. V, Ca, and Ti were excited by ^{55}Fe. Cr, Mn, Fe, Co, Ni, Cu, and Zn were irradiated with ^{238}Pu. Hg, Pb, As, Br, Sr, Zr, and Mo were excited by ^{109}Cd.

The automated x-ray fluorescence measurements required approximately 0.2 hour for operator and 0.45 hour for equipment operation. Good precision, accuracy (data compared with atomic absorption spectrophotometric analyses) and speed are attainable. A major time-consuming step in the analytical procedure is the weighing of the cellulose filter before and after collecting the sample. Also, due to the hygroscopic nature of the cellulose filters, they must be stored for 24 hours in a constant humidity box before each weighing and must be weighed a fixed time (7 minutes) after removal from the box. Additional operator time is required to cut out a 47-mm diameter disc from the 8" x 10" Whatman filter paper.

Giauque (ref. 90) developed a technique for experimentally substracting iron interference of Mn and Co observed in non-destructive x-ray fluorescent analyses of glasses and ceramics. By using an analyzer with a radioisotope source-target assembly (As K x-rays excited from an As_2O_3 target by an ^{241}Am source) and a Si(Li) semiconductor detector, detection limits $\leq$ 100 ppm Mn are attained. The interfering Fe peak was subtracted by exciting a pure piece of Fe metal with the analyzer in a subtract mode.

Frankel and Aitken (ref. 91) reviewed recent developments in energy-dispersive x-ray emission spectroscopy with particular emphasis on the solid state Si(Li) semiconductor detectors. The improved resolution attainable with the Si(Li) provides the means to distinguish between adjacent elements, e.g., Cr, Mn, Fe, Ni, Cu, Zn. Resolution attainable by crystal spectrometers equipped with scintillation counters, proportional counters, and ionization counters is not sufficient to provide comparable separation.

A portable fluorescent x-ray instrument (approximately 10 lbs and 0.5-1 ft^3) utilizing bremsstrahlung radiation from (a) tritium absorbed in zirconium or (b) promethium-147 was developed by Karttunen et al. (ref. 92,93) to measure elements in the range $Z = 16$ to 35. Analyses for macro amounts of Cr, Ni, V, Mn, and Cu are reported for alloys and cement. Although the resolution was adequate for the samples, the newer semiconductor detectors would be required to detect lower concentrations.

Yamamoto (ref. 94) applied an x-ray spectrometer with a Si(Li) semiconductor detector and an ^{125}I radioisotope source to the analysis of low-weight nickel samples. A detector limit for Ni of 1 μg is reported. An excellent discussion of the instrument parameters that affect the intensity of the analytical emission line is presented.

A high analytical efficiency, which is independent of the composition and density of the sample and of the measurement geometry, can be attained by using two monochromatic radioisotope sources in sequence (ref. 95). The energies of the two sources must be such that the energy of the other is slightly higher than that needed to excite the K-radiation from the element to be determined. ^{49}V and ^{55}Fe were used to determine V.

Si(Li) semiconductor detectors can provide the resolution necessary to separate adjacent atomic numbered elements, e.g., Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn. However, the additional cost of the device, and the maintenance of operation (liquid nitrogen coolant) may limit the application as a stack monitoring device. An alternate method of attaining suitable resolution is based on spectrum analysis by means of filters and radioisotope excitation sources (ref. 96).

The technique combines the simplicity of nondispersive systems with the resolution of complex dispersive equipment. Fluorescent radiation from a specimen, excited by means of a radioactive source, tritium/Zr, is measured after transmission through each member of a sequence of filters consisting of elements of consecutive atomic number. This provides a scan of the radiation by means of the absorption edges of the filters.

Disadvantages owing to interference in certain cases can be overcome by the use of suitable standards. Advantages of this nondestructive method are that it avoids complex instrumentation, elements of adjacent atomic number can be resolved, and no interference effects owing to target material can occur. Moreover, source stability is accurately assessable and corrections for lost counts are free from form factor calculations. In addition, the method is exempt from the effects associated with higher diffracted orders. The principle is applicable to solids and liquids, metals, nonmetals, conductors, nonconductors, or radioactive specimens. It has been applied to determine Mn in aqueous solutions over a concentration range of 0.7-21.0% Mn. A detection limit of 0.7 ppm Mn is estimated.

Rhodes, et al. (ref. 97) described a system using radioisotope x-ray fluorescence techniques and differential thin foil filters to isolate the characteristic radiation of Zn and Cu. The excitation source was ^{109}Cd and the ZnK x-rays were selected by Cu/Ni filters, whereas the CuK x-rays were isolated with Fe/Ni filters (Co/Ni could also be used).

A high-efficiency x-ray spectroanalyzer is described which is equipped with a ^{147}Pm β-ray source and a Xe-CH_4-filled proportional counter (ref. 98). Unwanted scattered β-rays are eliminated with a Be foil filter. K x-rays for the elements from Cr to Zn are used for analysis.

The intensity of the K_α line of Cu, as excited by a ^{3}H/Zr source, was measured by means of a proportional counter. Fe absorbs the measured x-rays and so lowers the results. The interference by Fe can be corrected after measuring the intensity of the K_α line of Fe or by using nomograms. In the absence of interfering elements and at the accuracy of the x-ray intensity measurement of 5-10%, the Cu content of 0.15-1% can be determined with an absolute error of 0.05-0.1% Cu (ref. 99).

A radioisotope x-ray fluorescence and preferential absorption method for the analysis of copper in mineral products was described by Ellis, et al. (ref. 100). For the copper-iron-lead-zinc minerals, considerable difficulty was encountered with the Cu analyses. The methods for compensating for changes in matrix composition were not suitable. The presence of zinc and lead complicated the correction for absorption effects. X-rays of energy under the zinc K absorption edge minimized the effect of zinc and lead. Changes in the iron content produced variations in the absorption of x-rays by iron and resulted in marked changes in Cu K x-rays. This effect was minimized by using a detector filter of suitable thickness. The error in the Cu determination was further reduced (halved) by compensation using an analysis for zinc. A Pu-238/Ga gamma-ray excited x-ray source and a 23 mg/cm^2 Cu filter was used.

A nondispersive two-channel x-ray fluorescence apparatus with two filters and two proportional counter detectors was developed by means of which the ratio of intensities of characte - istic emission in two spectral regions isolated by the channels can be measured and the differences in intensity determined by the method of balanced filters (ref. 101). Fluorescence of the samples is induced by the emission of a tritium/Zr radioisotope source. In determining copper in a brass matrix, a Cu foil filter was placed in front of one of the counters and a Ni foil filter in front of the other. The absolute variance of determinations of Cu was ±0.25% for measuring times of 8 minutes.

A method was developed to minimize the matrix effects on calibration curves (ref. 102). The method uses measurements at two wavelengths, one on either side of an absorption edge for the element under study. A development of the Beer's law expressions through subtraction of the absorbtivities at the two wavelengths (equal intensities are assumed for the two primary beams) leads to a linear calibration curve. The intercept of this curve is related only to the density and absorption properties of the matrix, while the slope is a linear function of the intercept and the absorption properties of the element. Once the slope of the calibration curve has been determined for an element in one matrix, a calibration curve in another matrix can be determined with only absorption measurements on the new matrix itself.

If the density and composition of the new matrix are known, the total calibration curve can be calculated without absorption measurements. The two wavelengths are obtained from K_α and K_β radiations from an element just higher in atomic number than the element analyzed, by using the target element or one of its compounds in the sample position. The K_α and K_β radiations are resolved with an appropriate analyzing crystal. Good agreement was obtained between calculated and experimental results. For example, analysis of Ni over a concentration range 0-1.5 wt.% had a standard deviation of about 0.03%.

Two portable x-ray fluorescence analyzers, based on radioisotopic excitation and isolation of fluorescent radiation by pairs of balanced absorption filters, have been developed. The instruments weigh between 12 and 16 pounds and are useful for detecting elements having atomic number >20. Sources and filter pairs useful for Ti, Fe, Cu, Zn, Mo, Sn, Pb, Cr, Mn, Ni, Zr, Ba, and W are reported (ref. 103).

Hans (ref. 104) analyzed plant stream samples automatically with x-ray fluorescence for Cu by minimizing mutual interferences of Co and Cu with dilution techniques and addition of concentrated sulfuric acid.

3.5 Neutron Activation Analysis

Main virtues of neutron activation analysis (NAA) are sensitivity and freedom from reagent contamination problems. A typical NAA analysis consists of four steps: irradiation of the sample, chemical isolation of the element sought, measurement of the activity, and evaluation of the results. The most time consuming of these steps are the chemical isolation of the element to be measured and the cooling time to minimize interfering radiation prior to measuring activity.

Another limitation of NAA is the massiveness of the conventional neutron sources. The limitation is somewhat alleviated by using radioisotope sources which also permit on-stream detection of V, Mn, In, Se, Al, F, and U.

Nondestructive neutron activation analyses of particulate collected from ambient air have been reported for the Chicago area (ref. 105, 106). Particulate collected on cellulose filters over a period of 24 hours was analyzed for manganese, vanadium, chromium, and other elements after irradiating the specimen with thermal neutrons. Irradiation exposures were 1 minute and 24 hours (for long-lived nuclides). Cooling times, prior to counting, were as long as 1, 2 and 9 months after irradiation. Concentrations of 2-120 ng V/m^3 of air, 6-37 ng Cr/m^3 of air, and 100-900 ng Mn/m^3 of air are reported.

When doing neutron activation analysis of particulate collected on filters, consideration must be given to the physical properties and elemental composition of the filter itself. A practical aerosol filter for routine use must be easy to handle, have high collection efficiency, and be low in price. Commonly used fiber glass and asbestos-base filters cannot be used because of high background. Millipore and Microsorban have acceptable backgrounds but are expensive, fragile and hard to weigh due to static charges. Variability in background from batch to batch is characteristic of Microsorban. Cellulose-base filters are easy to handle, are low in price, and have a low background. Unfortunately, the collection efficiency is low; two filters in series are required (ref. 106).

A nondestructive and computer assisted neutron activation analytical procedure for determining up to 33 elements including Cr, Cu, Mn, Ni and V in air pollution particulates was developed and tested in ambient air studies near the Northwest Indiana industrial area (ref. 107). Polystyrene filters were used because of low background signals. Each specimen was irradiated for five minutes at a flux of 2 x 10^{12} neutrons/cm^2sec. After suitable decay times, the following detection limits in absolute values (μg) and in concentration in urban air (μg/m^3) for a 24-hour sample were obtained: V @ 3 min decay time (0.001 μg; 0.002 μg/m^3); Cu @ 3 min decay time (0.1 μg; 0.02 μg/m^3); Mn @ 15 min decay time (0.003 μg; 0.0006 μg/m^3); Cu @ 20-30 hr decay time (0.05 μg; 0.005 μg/m^3); Cr @ 20-30 day decay time (0.02 μg; 0.00025 μg/m^3); Ni @ 20-30 day decay time (1.5 μg; 0.02 μg/m^3).

Pillay, et al. (ref. 108) developed a nonisolative (nondestructive) neutron activation analysis procedure for determining the concentration of 16 elements in airborne particulates collected in Buffalo, N.Y. area. The procedure involved multiple neutron irradiation and high resolution gamma-ray spectrometry.

Short-lived isotopes produced by thermal neutron irradiation (5 minutes) of manganese and vanadium could be measured immediately. After irradiating a second time for two hours and permitting a decay for 8 to 12 hours, manganese, and copper were determined. A third irradiation for 24 hours with a decay period of 5 to 7 days was required to measure chromium and nickel. Also, since the filter paper was damaged by irradiation during the third irradiation, an extraction step with nitric acid was required.

Air particulate contains a large number of elements that can interfere with the analyses. However, by using activated standards and by calibrating the detector-analyzer [semiconductor-Ge(Li)] system with a large number of known isotopes, the interferences are overcome (ref. 108).

Activation analysis detection limits are generally expressed on an interference-free basis. Typical values on an interference-free basis for selected elements are as follows: B (1.1 μg), Ba (0.02 μg), Cr (0.3 μg), Cu (0.002 μg), Mn (0.0001 μg), Ni (0.7 μg), and V (0.002 μg). However, during nondestructive activation analyses, i.e., no radiochemical separation, where interferences can occur, a commercial neutron activation analysis service reports detection limits as follows for an air particulate sample (14 mg): Cr (18.0 μg), Cu (1.10 μg), Ni (190 μg), V (2.30 μg). Less problems were observed with Ba and Mn.

Wyttenbach (ref. 109) performed nondestructive NAA on powdered rocks, cements, and meteorites for V, Mn, and other elements with irradiation times below one minute and counting times below five minutes on specimens 10-40 mg. The reproducibility of V results is influenced by the Mn and Al concentrations. With Al, a critical weight ratio, V:Al = 5 x 10^{-3} was observed. (Undoubtedly, this effect can be alleviated somewhat by a detector system - semiconductor, Ge(Li) - that has better resolution). Grain size >150 mesh presented a problem since the specimens used were inhomogeneous.

Mean concentrations of Mn (0.033 μg/m^3) and V (0.015 μg/m^3) were measured by NAA and gamma-ray spectrometry in airborne particulates (ref. 110). The technique is nondestructive, and is most suitable for those elements which have a large neutron activation cross section for the production of isotopes which decay with the emission of γ-rays of high abundance and have convenient half-lives (1 min. to 1 day). Irradiation time of 5 minutes resulted in detection limits of Mn - 0.0003 μg/m^{-3} and V - ~0.001 μg/m^3 for an air sample drawn through 20 cm^2 of a glass fiber filter. The V detection limit was influenced by the masking of the γ-ray spectrum by other elements. [Note - A NaI(Tl) scintillation detector was used. Better resolution and potentially less interference would be attained with a semiconductor detector.]

With Ge(Li) γ-ray detectors better resolution is possible than that obtained with NaI(Tl) scintillation counters previously used for γ-ray spectrometry (ref. 111). By irradiating for 5 minutes, particulate collected on filters can be analyzed for V, Mn, and other elements without destruction of the sample. The best times after irradiation for counting are 0-20 minutes for V and 1-4 hours for Mn. Detection limits for samples (20 to 50 m^3 of air) collected for 12 hours are V - 5 x 10^{-4}μg/m^3 and Mn - 0.001 μg/m^3.

Generally neutron activation analysis (NAA) methodology uses gamma-ray spectroscopy as the means of detecting over 70 elements and steady state irradiation to induce activity. However, poor sensitivity is usually encountered with short-lived radionuclides.

Improved sensitivity can be attained by using short-lived radionuclides - including some pure beta emitters and some with half-lives of one second or less - in NAA with high intensity reactor pulses and a combination detector system, which includes both a NaI(Tl) detector and a Cerenkov detector (ref. 112).

Samples were irradiated with pulses of 10^9 watt peak power and 16.6 milliseconds (FWHM) deviation. Under these conditions, the thermal- and fission-spectrum peak neutron fluxes were 1.1 x 10^{16}n cm^{-2}sec^{-1} and 2.1 x 10^{16}n cm^{-2}sec^{-1}, respectively. These can be compared with thermal- and fission-spectrum neutron fluxes in the steady-state irradiations (250 KW) of 2.5 x 10^{12}n cm^{-2}sec^{-1} and 5.3 x 10^{12}n cm^{-2}sec^{-1}, respectively.

The technique can be applied to the measurement of B, Be, Li, O, F, Mg and Pb. With this sytem, the following detection limits were attained: B - 1.1 μg, Be - 15 μg, Li - 0.0008 μg, O - 370 μg, F - 0.83 μg, Mg - 160 μg and Pb - 0.4 μg. The detection limits for B, Be, and Li are superior to those reported by steady state irradiation techniques whereas the detection limits for F and Pb are comparable to, but those for O and Mg are poorer than previously reported limits. The technique is rapid, but limited in the analytical time requirements by the need of having a weighed specimen.

The detection of Cu by activation analysis is dependent on other elements, particularly Na, capable of activation. By using computer techniques for analyzing gamma-spectra, a practical limit of detection for copper in a sodium containing matrix corresponds to a Na/Cu ratio of 100.

The fact that ^{64}Cu is one of the few positron-emitting nuclides produced by thermal neutron activation has led to the use of 180° annihilation quanta for gamma-gamma coincidence measurements. The application of this technique to a number of matrices is shown by Michelsen and Steinner (ref. 113). For the concentration range, 50-650 ppm Cu, in geological samples having a Na/Cu ratio of 3.3 to 330, the relative standard deviation ranged from 2.0-6.4% for 10-minute counting times. Good agreement with other analytical techniques are reported. The spread of replicate determinations was reported as due to counting errors and errors due to neutron flux inhomogeniety in the irradiation position. Possible interference from the nuclear reaction ^{61}Zn(n,p)^{64}Cu might be significant, but becomes important only if the zinc content is 100 times higher than the copper content.

Boron has been measured successfully by the ^{11}B(p,γ)^{12}Cu reaction after irradiation with 900-keV protons (ref. 114). At this energy level the only interfering element is Li, but its effect can be eliminated by using resonance reaction with 163-keV protons.

Several nondestructive neutron activation methods (ref. 115, 116) are based on the activation of ^{10}B (natural isotopic abundance of 19%). By using the ^{10}B(n,α)^{7}Li^{m} reaction, α particles can be measured with an Au-Si surface barrier detector or after de-excitation of the excited state; Li nuclei γ-quanta can be measured with a Ge(Li) detector. Irradiation with neutrons can be accomplished with an Am-Be neutron source (1Ci).

Increased differentiation between elements by nondestructive activation analysis can be obtained by using fast neutrons from an isotopic source, rather than by using thermal neutrons. Activation analysis by isotopic neutrons is suggested as being superior in certain applications for selected elements, e.g., in assaying geological specimens. Ming and Wahlgren (ref. 117) report the sensitivities (counts per gram) with fast neutrons from an ^{241}Am-^{242}Cm-Be source. For sensitivities of 10^{3}-10^{5} counts/g, the irradiation times, cooling times, and counting for selected elements are: V - 15 min, 4 sec, 15 min; Cr - 15 min, 4 sec, 15 min; Mn - 15 min, 4 sec, 15 min; Ni - 1 hr, 100 sec, 1 hr; Cu - 15 min, 4 sec, 15 min; Ba - 10 min, 4 sec, 10 min.

Boron and other elements, which cannot be detected by steady state thermal neutron activation analysis, can be determined by using half-lives between 0.55 and 873 msec with 14-MeV neutrons. A pulsing technique is used (ref. 118).

Activation in linear accelerators or fixed or variable energy cyclotron can result in the detection of 10^{-9}g of B, C, N, O, and F. Deuteron activation is used for trace amounts of B (ref. 119, 120).

Gamma spectrometric measurement of a boron-containing sample by a modulated neutron beam permits the determination of the short-lived product ($T_{\frac{1}{2}} = 5 \times 10^{-14}$sec) of the $^{10}B(n,\alpha)^7Li^m$ reaction. To obtain quantitative results, an internal standard (samarium) is necessary to overcome variations in reactor flux and the asymptotic relationship between concentration and count rate for materials of high cross section (B) (ref. 121).

The detection of traces of V in flowing aqueous systems has been determined by continuous activation by fast neutrons. Large volumes of solutions were activated and the gamma component of induced radiation was measured. Suggested applications include detection of F, V, and U by on-stream monitoring of industrial effluent (ref. 122).

Kartashev and Shtan (ref. 123) developed a similar on-stream, continuous, automatic, neutron activation system for V, Mn, In, Se, Al, and F by using a ^{239}Pu-Be source.

By using a ^{124}Sb-Be source for on-stream activation analysis, V, Mn, Al, Hf, In and Ag were determined repetitively in 5-10 min cycles at <100 ppm. Additional data are given for Cl, Co, Mg, Na and Cu (ref. 124).

3.6 Colorimetry

Numerous spectrophotometric methods are available for measuring B, Ba, Cr, Cu, Mn, Ni, and V as trace elements in various media. For measuring these elements, digestion processes (ashing, acid extraction, and possible complexation) are necessary. Because of the lengthy time elements involved, most spectrophotometric methods are not applicable to continuous or short-term intermittent measurements. Information in the following subsection is reported as related to potential problems involved in applying spectrophotometric methods, or to methods providing high sensitivity, specificity or high degree of automation.

The spectrophotometric technique (diphenylcarbazide) for determining chromium in air as particulate collected on cellulose or glass-wool filters may produce erroneous results due to low recovery of Cr(∿60%). The low values result from partial reduction of Cr(VI) to Cr(III) (ref. 125).

An automated spectrophotometric method for Cr has been developed based on catalysis of Cr(VI) of the reaction between aqueous H_2O_2 and I^- in H_2SO_4. The time required for producing a small fixed amount of I_3^- is found by automated measurement of the extinction at 365 nm and is proportional to the Cr(VI) concentration. Na, K, Mn(II), Ni, Cl^-, and NO_3^- do not interfere, but oxidizing and reducing agents do. From 0.6 to 3.0 μg of Cr(VI) can be determined to within ±1 to 2% in 10 to 50 sec (ref. 126).

An automated solvent extraction, colorimetric method for determining Cu has been developed based on forming the diethyldithiocarbamate or dibenzyldithiocarbamate and using a Technicon Autoanalyzer. The method enables 15 samples/hour to be handled with precision comparable to corresponding manual methods (ref. 127).

A kinetic method for V based on the catalytic effect of V on oxidation of I^- by BrO_3^- has been used to measure the concentration of V within the range 0.01 to 100 ng per ml. The rate of reaction (measured photometrically) is directly proportional to concentration of V (ref. 128).

Brief, et al. (ref. 129) summarize methods for collecting and analyzing air streams for nickel carbonyl and report a detailed development of the thermodynamics associated with the formation of nickel carbonyl. The various methods evaluated for collecting and detecting nickel carbonyl include:

(1) Collection - Absorption in saturated solution of sulfur in trifluoroethylene
Detection - Emission spectrography
Detection Limit - 0.0003 ppm

(2) Collection - Reaction with mercuric oxide to form Hg°
Detection - Mercury vapor photometer
Detection Limit - 0.0014 ppm

(3) Collection - Absorption in acidified solution of chloramine-B in alcohol
Detection - Colorimetric using dimethylglyoxime
Detection Limit - 0.01 ppm

(4) Collection - Reaction with iodine in CCl_4
Detection - Colorimetry-dimethylglyoxime determination
Detection Limit - 0.1 ppm

(5) Collection - Reaction with dilute sulfuric acid
Detection - Spectrophotometry-sodium diethyldithiocarbamate
Detection Limit - No data

Brief, et al. (ref. 129) propose a method for nickel carbonyl in which air or process gas is bubbled into 10-15 ml of 3% aqueous

HCl solution in a midget impinger for 30-60 minutes at 0.1 ft^3/min. A filter assembly preceding the bubbler removes nickel solids. After pH adjustment, color formation is developed with alpha-furildioxime and the resultant colored complex is extracted into chloroform to be measured spectrophotometrically.

Other collection media for nickel carbonyl include ICl in acetic acid and alcoholic or ethereal iodine solution. For continual determination of $Ni(CO)_4$ in the gas phase, the use of absorption spectrophotometry is reported, but no data are given (ref. 130).

A very sensitive, continuously recording nickel carbonyl detector was developed based on the thermal decomposition (350°C) of nickel carbonyl on a borosilicate glass plate. The reflectance of polarized light incident at the Brewsterian angle for the glass is measured by a recording photomultiplier photometer and correlated with the concentration of nickel carbonyl (ref. 131). The critical parameters are the rate of sample flow (500 cc/min) and the rate of rotation of the glass disc on which the deposit is formed. With a 5-minute deposition tiem, a detection limit of 0.2 ppm is attainable; with a 10-minute time, a detection limit of 0.05 ppm is observed.

The system is also sensitive to iron carbonyl and could be adapted to detection of alkyllead compounds and other metal-organics.

A multiple dilution system for generating known concentrations of nickel carbonyl is also presented (ref. 131).

By sampling 100 cc of air or other test gases containing nickel carbonyl @ 1 cc/sec, color development can be induced in silica gel containing 0.5% $AuCl_3$. Adjustment of the sample volume permits a measuring range of 3-2000 ppm of $Ni(CO)_4$ (ref. 132). Silica gel impregnated with KIO_3 in H_2SO_4 has also been used to determine $Ni(CO_4)$ vapor in the atmosphere (ref. 133).

Draeger tubes are available that measure $Ni(CO)_4$ in the range 0.1-1 ppm (ref. 134).

An evaluation (ref. 135,136,137) of a number of methods for determining chromic acid mist in air indicates that a filter paper procedure is the most suitable for a rapid field method in preference to methods employing sampling liquids. By using a thick (0.026-in.) absorbent paper, an efficiency of 99.9% was attained by drawing air through the filter with a hand pump. A reagent mixture of 4% phthalic anhydride and 0.25% s-diphenylcarbazide in 95% ethanol and 20 ml of glycerol per 100 ml of reagent is used to prepare the impregnated paper discs. By visual comparison with dye standards in the field, a 600-ml air sample can yield results within 0.5 mg/m^3 for concentrations below 3.3 mg/m^3.

A direct, specific, determination of decaborane in air can be attained by absorbing the decaborane as a soluble red adduct with quinoline in xylene (ref. 138). High collection efficiencies were obtained at gas flow rates of 0.5 l/min and concentrations of 1 to 25 μg of decaborane per milliliter of solution can be determined conveniently. Neither diborane nor pentaborane interfere.

Two instruments - a portable, field model with a hand-operated pump and a continuous recording analyzer - based on the nonspecific reduction of triphenyltetrazolium chloride by boron hydrides have been developed (ref. 139). Metered air samples are passed through filter paper or cloth tape impregnated with reagent. The red color produced is measured by visual comparison techniques in the field model and by a differential reflectance photometer with the automatic instrument. Although relatively insensitive to diborane, 0.1 to 0.5 ppm of decaborane and pentaborane can be detected. (Note - It is important to understand that the reaction is not specific to boranes and that a large number of reducing agents could interfere with the method.)

Fristrom et al. (ref. 140) concluded after evaluating available analytical techniques that there is no quantitative detection means applicable directly to all the volatile boron hydrides and their organic derivatives in the range of their maximum allowable concentrations. As a consequence, a monitoring unit was developed in which boron hydride vapors are burned in air and the solid products (boric oxide and boric acid) are collected and analyzed as solutions with a carmine colormetric (manual) method. Best colorimetric results were obtained on solutions containing 1 to 10 μg B/ml. Sampling flow rates of 0.5 liter/min yielded 30 μg B as B_2O_3 (6 μg/ml H_2O) in 30 minutes from air containing 1 ppm pentaborane.

3.7 Polarography

Particulate from air collected on Millipore filters or glass fiber filters has been analyzed for Cu, Cr, Ni, and Mn and other trace metals by polarographic techniques (ref. 141). Although relatively high sensitivity (10 μg) and reasonable specificity is attained, the preliminary sample preparation, which entails wet or dry ashing (removal of organics) and acid extraction, is time-consuming.

3.8 Back-scattering of β-radiation

Back-scattering of β-radiation from ^{90}Sr-^{90}Y by Ba in ores and concentrates has been used to measure Ba content (5-94%) with

0.2-5.0% relative error if samples and standards are ≤20μ grain size, constant density, and constant moisture. Interference (soft backscattered β-radiation) by elements with atomic number ≤26 was eliminated by using an Al filter (ref. 142).

3.9 Mass Spectrometry

One of the major limitations of applying spark source mass spectroscopy to particulate collected from ambient air or stack emission is the fact that nonconducting materials cannot be used as self-electrodes. The nonconducting powdered sample must be mixed with a conductor, e.g., graphite.

Evans, et al. (ref. 143) demonstrated an analytical method using a spark-source mass spectrograph equipped with an electrical detection system. With reproducible sample positioning, Cr, Mn, V, and other elements were measured in stainless steel standards with precision of ±3% and accuracy of ±7%. The major problems are (a) spark-electrode instability, (b) sample or instrument turnaround, including mounting, chamber evacuation, and prespark (Note - requires approximately 15 min/sample), and (c) restrictions of mass range since only a M-2M mass range can be covered. (Note - Restrictions on accelerating voltage are maintained to provide sensitivity and good ion extraction efficiency. Approximately 15 min is required to find a new mass range, allow the magnetic field to stabilize, and set proper peaks on the electrostatic peak switcher.

A typical analysis for up to five elements (within M-2M) per sample would require (a) 30-min peak setup and analysis of standard per day and (b) 20 min/sample for a total of 21 samples and 105 determinations per 8-hr day. For analyses requiring measurements for a wide mass range of elements [assuming 4 groups of 5 elements (C to Bi)], approximately 100 determinations per 8-hr day are predicted (ref. 143).

Brown and Vossen (ref. 144) developed a special analytical technique for collecting particulate from ambient air and for determining all elements from atomic number 92 (uranium) to atomic number 3 (lithium) in one scan with a spark source mass spectrometer. The mass spectrometer is fitted with an electrical detection system which permits a measuring time of 9 minutes plus set-up time between analyses of 10 minutes.

Particulate is collected for 9.5 hours @ 19 liters/minute on a nitrocellulose filter pad which is ashed to prepare a specimen for the mass spectrometric measurement. The total weight of sample retained on the pad was two milligrams and the following concentrations of elements were reported: B - 0.004 μg/m^3, Ba - 0.02 μg/m^3, Cr - 0.30 μg/m^3, V - 1.9 μg/m^3, Mn - 0.07 μg/m^3, Ni - 0.32 μg/m^3, and Cu - 0.26 μg/m^3.

No data on repeatability, accuracy, etc., are shown. The work is principally a preliminary feasibility study.

Bratten and Wood (ref. 145) studied the changes of relative sensitivity coefficients for Cu, Cr, Mn, and Ni with concentration and matrix in measurements performed with spark-source mass spectrometry. Cr and Cu reveal little or no concentration or matrix effects down to 0.08% in nickel- or iron-base matrix. However, Ni seems to produce considerably higher factors as the concentration drops below 100 ppm. Conversely, coefficients for Mn decrease sharply below a few tenths of a percent.

Reasonable agreement between spark source mass spectrometry and neutron activation analysis for Cr, Cu, Ni and other elements have been observed in forensic applications (ref. 146). Poorer agreement is observed for Mn, Ba, and Ti; spark source mass spectrometric analyses are higher. There is the possibility of a hydrocarbon interference for Mn, Ba and Ti in the mass spectrometer data.

Mass spectrometry has been used to measure boron indirectly by determining the number of helium atoms produced in the thermal and epithermal $^{10}B(n,\alpha)$ reaction (ref. 147). The detection limit of B varies with the type of sample; in steel, concentration below 10^{-5}% B in samples of 0.1 to 1 g can be determined.

Other mass spectrometric methods, based on stable isotope dilution have been applied to the determination of trace metals. A typical example (ref. 148) is the method as applied to trace amounts of chromium. The sample is dissolved in hydrochloric acid containing a small portion of tracer solution, oxidized with nitric acid and heated to fumes with sulfuric acid, and the chromium(III) is then oxidized to chromium(VI) with cerium(IV) sulfate. The chromium(VI) is extracted into isobutyl methyl ketone in N hydrochloric acid and is then back-extracted into water. The solution is deposited on a rhenium filament and dried. The deposit is vaporized in the source of the mass spectrometer and the peak intensities in the mass range 51 to 54 are measured.

One of the major advantages of isotope dilution-mass spectrometry is that once isotope exchange has taken place there is no requirement for quantitative or "clean" separations.

The isotopic dilution method has been to the determination of boron in silicon and zirconium (ref. 149). By adding 1:1 glycerol-NaOH or 1:3 mannitol-MeOH to the isotopic-dilution matrix, a stable, intense beam is obtained.

The determination of Cu at ng levels, as its acetylacetonate complex, by electron impact mass spectrometry is reported (ref. 150). The method requires dissolution of the copper containing material, formation of the acetylacetone complex, and addition of a completely deuterated complex as an internal standard. The error of the method is ∿3%.

Booker, et al. (ref. 151) reports the quantitative measurement of 0.5 to 200 ng of Cr by mass spectrometric analysis of chromium(III) hexafluoroacetylacetonate. The metal chelate is prepared by digesting the specimen with perchloric acid followed by chelation with hexafluoroacetone. Although highly sensitive, the analytical procedure requires over eight hours for the digestion and chelation steps.

3.10 Chemiluminescence

Although no analytical method has been reported based on chemiluminescent reaction of nickel carbonyl with ozone, the kinetics and mechanism studied by Morris and Niki (ref. 152) suggest that a very sensitive, continuous, analytical method based on this phenomenon may be attainable. NiO emission was observed with $Ni(CO)_4$ and ozone only in the presence of carbon monoxide. With only ozone and nickel carbonyl, a nonluminous reaction occurs, but the NiO emission can be generated by adding carbonyl-free CO downstream. Iron carbonyl may interfere but the kinetics of the decay of FeO and NiO emission are quite different; also, the formation of NiO emission in ozone from nickel carbonyl requires CO, whereas the formation of FeO emissions from iron carbonyl does not.

Small amounts (down to 0.05-5 ng/ml) of Mn in any oxidation state and in the presence of activators catalyze the oxidation of luminol by H_2O_2. The resulting increase in chemiluminescence is a measure of the Mn concentration. Fe, Co, and Cr interfere in high concentration, but the Fe interference can be prevented by UV radiation of the mixture before adding luminol (ref. 153).

Chemiluminescent reactions involving luminol-metal (Cu)-H_2O_2 and similar reactions with V permit the detection of 10^{-9}g of metal (ref. 154).

3.11 Coulometry

A continuous, automatic coulometric titration system was devised to monitor boranes in air (ref. 155). Boranes absorbed from air into a sodium bicarbonate-potassium iodide electrolyte are titrated with coulometrically generated iodine. Detection limits as low as 0.2 ppm by volume of diborane and decaborane in air are attainable. Theoretical limits are concentrations of 0.01 ppm by volume. All boranes react in the same way with the iodine. At air flow rates of ∿0.420 liter/minute, collection times of 15-20 minutes were used to measure 0.24 to 0.28 ppm decaborane and collection times of approximately 45 minutes and 90 minutes were used to measure 1.02-1.08 ppm and 0.48 ppm of diborane, respectively.

Acetone, peroxides, H_2S, ozone, and nitrogen oxides interfere; methanol, methyl borate, boric acid, benzene, butene and hydrogen do not interfere (ref. 155).

3.12 Polymer-Radiographic Methods

Although the practical application of an autoradiographic method (ref. 156) for determining trace quantities of boron (<1 ppm) in solids in collected airborne or stack emission particulate is questionable, the approach requires description. Since cellulose acetobutyrate films will record α-particles only up to 1.5 MeV, a moderately specific method for determining trace quantities of boron may be devised based on this phenomenon.

The technique is based on measuring the density of tracts in the acetobutyrate film produced by the alpha particles generated in the $^{10}B(n,\alpha)^7Li$ reaction during irradiation of specimens with a thermal-neutron flux.

Too much analysis time is required to perform the steps of irradiating, forming a replica, heat-treating, and etching to use the technique as it exists now as a monitoring method.

However, some small consideration should be given to the feasibility of using polymers sensitive only to alpha particles or proton tracks to detect B or other elements having isotopes with large cross-sections for (n,α) or (n,p) reactions. By using an impact collection device with an α or proton sensitive polymer, a portable radioisotope neutron source to promote the (n,α) or (n,p) reaction, and a light obscuration system, a semi-continuous monitor may be possible. The principal limitation may be lack of sensitivity of the polymer to the desired radiation resulting in inordinate exposure or developing times.

3.13 Gas Chromatography

Sunderman, et al. (ref. 157) developed a gas chromatographic method for nickel carbonyl in blood and breath. The nickel carbonyl in breath (0.5 µl/l) was trapped in ethanol and subsequently analyzed by gas chromatographic means. The procedure has value for measuring industrial exposures or plant emissions since the method differentiates between $Ni(CO)_4$ and less toxic Ni compounds.

The major limitation is the need to collect the $Ni(CO)_4$ in ethanol. A direct sampling procedure or a preconcentration step on a section of gas chromatographic packing which could be temperature programmed for desorption of $Ni(CO)_4$ into the analytical column would be a more attractive procedure for an intermittent monitoring system to measure $Ni(CO)_4$.

3.14 Reaction of Nickel Carbonyl With Mercuric Oxide

Brief et al. (ref. 158) summarized a continuous method developed by Voll'berg (ref. 159), in which air containing nickel carbonyl is drawn through mercuric oxide at 200°C and liberated elemental mercury is measured spectrophotometrically. A parallel stream of air containing nickel carbonyl is drawn through an oxidizing reagent to convert nickel carbonyl to carbon dioxide. This effluent is then passed over mercuric oxide and the liberated elemental mercury is determined spectrographically. The difference in the amounts of mercury vapor obtained is a measure of the nickel carbonyl in the air. A sensitivity of 0.0014 ppm is reported.

4. SUMMARY AND RECOMMENDATIONS

At this time, there is no continuous monitoring system for stationary source emissions which measures B, Ba, Cr, Cu, Mn, Ni, and V as individual elements or in a multi-element functional model. Most laboratory techniques to date have been applied to integrated samples of particulate collected on filter paper from ambient air.

High sensitivities and the attendant low detection limits of the absorption and emission spectroscopic techniques make these techniques most attractive for continuous or short-term, intermittent monitors. By maintaining the element sought in the stack gas and by introducing the stack gas as part of the oxidant or fuel in the flame or high energy discharge of the excitation source of the spectrometer, a continuous monitoring system is possible. With B, Ba, Cr, Cu, Mn, Ni, and V, the major problems with using the absorption or emission spectroscopic techniques are the inter-element or compound formation effects.

With atomic absorption spectrophotometry, the inter-element or compound formation effects are minimized or eliminated by using a nitrous oxide-acetylene flame. The best results are obtained with a sheath gas (inert gas, e.g., nitrogen) to exclude oxygen from the flame. Obviously, in ambient air or stack emissions, elimination of the oxygen is extremely difficult. One possible way is to pass the stack gas or air over hot carbon to produce carbon monoxide.

The use of an inert gas plasma as an atomization source for atomic absorption spectrophotometry will also minimize inter-element effects if a reducing atmosphere is maintained in the plasma. The reducing atmosphere can be maintained by introducing hydrogen gas. An additional problem related to the use of a plasma to provide the atomization for atomic absorption measurements is the possibility of overexciting the element sought to emission, rather than to the necessary ground energy state. As a result, the population of ground state atoms may be too low to attain maximum sensitivity. Generally, the selection of the "viewing zone" of the plasma must be optimized depending on the element to be measured.

Although flame photometry can be used for measuring Ba and a number of other elements, inter-element and compound formation effects are also a problem. These effects can be minimized by using a nitrous oxide-acetylene flame.

Some inter-element effects are observed in arc- or spark-emission spectroscopy, but these can be eliminated by using high energy excitation, e.g., a radio-frequency plasma. Continuous monitoring systems for Be, Hg, and Pb, based on emission spectroscopy, have been developed using arc- or spark-excitation. Similar approaches with either an arc-or-spark excitation or a radio-frequency plasma can be applied to other elements. With a radio-frequency induced plasma, emission spectrographic analyses for B, Ba, Cr, Cu, Mn, Ni, and V without inter-element effects and on a continuous operational mode are possible. Repeated scanning of plasma induced emission lines of chromium and manganese show high stability as indicated by relative standard deviations of intensities of 1.9% and 1.7%, respectively, when the sample is introduced continuously as an aqueous solution.

X-ray emission (fluorescence) spectrometry is not applicable for measuring boron emissions. With a high resolution semiconductor detector, x-ray emission techniques with conventional x-ray target tubes and with radioisotope sources can be used on an intermittent basis to determine Ba, Cr, Cu, Mn, Ni, and V in particulate collected on filters. Care must be taken to measure thin film deposits so as to minimize matrix effects. Also, the background of secondary emission of x-rays from the filter media can be a major interference.

Radio-isotope sources for x-ray emission measurements provide a high degree of portability and simplicity of ancillary equipment. When applied to monitoring particulate collected on filters, good accuracy and repeatability of measurements are obtained. The major limitations in applying the x-ray techniques are the time to collect sufficient particulate on the filter and the potential loss of volatile emissions containing the element sought.

Nondestructive neutron activation analysis can be performed on particulate for certain elements, but not all. The major problem is the interference from radioactive isotopes of other elements. Lengthy cooling times ranging from several hours to several months are necessary to obtain sufficient sensitivity for some elements, particularly Cr and Ni. Manganese and vanadium can be measured immediately. Depending on the detection level required, copper can be measured immediately or, if a lower detection level is necessary, after 20-30 hr decay time.

By using high intensity reactor pulsing techniques, boron can be determined by nondestructive neutron activation analysis techniques, but not by conventional steady-state thermal neutron irradiation.

With fast neutrons from an isotopic source, much shorter irradiating and cooling times are possible. There is some sacrifice of sensitivity, but the technique provides for detecting Ba, Cr, Cu, Mn, and V in approximately 30 minutes total time. Measurement of Ni can be accomplished in approximately 2 hours.

Continuous, on-stream (aqueous solutions), neutron activation analyses of V and Mn have been performed with isotopic sources at the $\leq$100 ppm level in 5-10 minute cycles.

The chemiluminescent reaction of $Ni(CO)_4$ with ozone in presence of carbon monoxide deserves consideration as a possible system for continuous monitoring of $Ni(CO)_4$ emissions. Possible applications including monitoring: (a) effluent from the Mond process of refining nickel, (b) formation of $Ni(CO)_4$ when CO in effluent emissions passes over or through nickel products or alloys, and (c) losses of nickel metal particulate from filter media in particulate sampling systems.

In special cases, continuous colorimetric measures are possible for certain boranes. However, the application of the techniques must be made with care to ensure absence of interferences.

Measuring boron indirectly with mass spectrometry by determining the number of helium atoms generated in the $^{10}B(n,\alpha)$ reaction should be further evaluated.

Any technique relying on the collection of particulate on filters from relatively large volumes of air or stack gases risks the potential loss of volatile compounds. This is true even with relatively nonvolatile compounds, for example, chromic oxide volatilization can be enhanced by forming chromium trioxide in an oxygen atmosphere.

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APPENDIX VII

OPERATIONAL AND MAINTENANCE MANUAL
RF AND ARC EXCITED EMISSION SPECTROSCOPY SYSTEM

1. DESIGN CONCEPT

A relatively simple grating monochromator and optoelectronic detection system was coupled with two types of excitation sources - a radio-frequency (RF) generator and an AC arc discharge system - to form two test versions of a Be/Cd monitor based on spectroscopic measurement of optical emission from beryllium and cadmium. Two approaches were devised for producing the RF excitation. Instrumentation for both RF systems and the AC arc excitation mode are described in the following subsections.

The basic configuration of the spectroscopic systems was the same regardless of the excitation source, and the general schematic for the configuration is shown in Figure 1.

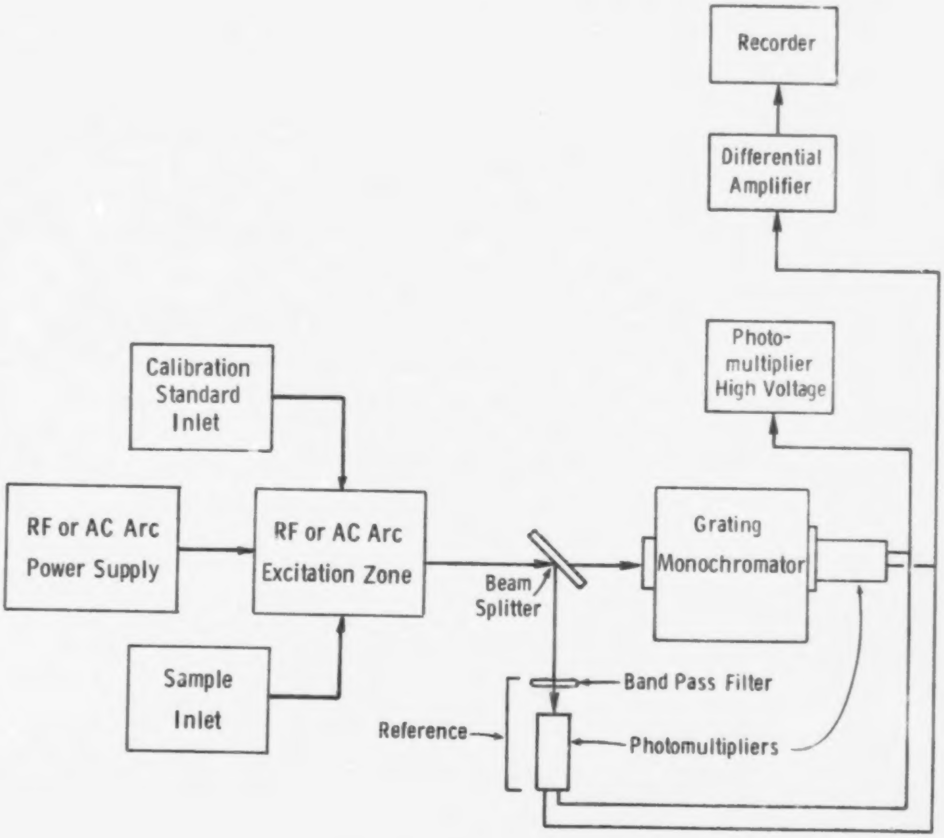
Recorder
Differential Amplifier
Photo-multiplier High Voltage
Calibration Standard Inlet
RF or AC Arc Power Supply
RF or AC Arc Excitation Zone
Beam Splitter
Grating Monochromator
Sample Inlet
Band Pass Filter
Reference
Photomultipliers

Figure 1. Schematic of Be/Cd Detection System Based on Radio-frequency Excitation.

Spectral emission from Cd and Be excited by the RF or AC arc induced discharge is isolated by a diffraction grating monochromator. The emission intensity of the spectral lines, which is a function of concentration, is measured by a photomultiplier detector and ancillary electronic read-out. A Jarrell-Ash quarter meter monochromator is used as the dispersive element in this arrangement (Figure 1). To ensure a high degree of source stability, a small fraction (∿1%) of the radiant beam emanating from the discharge zone is split off, a spectral band isolated by a band-pass filter, and the intensity of the band monitored by a photomultiplier detector. Small perturbations in the source, arising from discharge instability, etc., are "nulled-out" electronically by incorporating this type of reference channel in the electro-optical segment of the detector. This is accomplished by processing the signal from the reference channel and the analytical channel(s) through a differential amplifier. The optical band-pass of the reference beam is selected on the basis that it reflects a strong dependence on salient discharge parameters such as flow, pressure, power input, etc. Small changes in source intensity, consequently, are detected and subtracted from the analytical channel.

2. INSTRUMENTATION

2.1 Lepel Radio-frequency Generator

The Lepel generator is a vacuum tube type instrument designed to deliver an appropriate inductively coupled load 2.5 kilowatts (KW) of megacycle RF energy. The following specifications apply to the generator:

Power Output	2.5 KW
Operating Frequency	15-50 MHz, continuously variable
Input Voltage	230 VAC single phase
Full Load Current	25 amperes
Power Input	5.75 KVA
Cooling Water Pressure	Min. 30, Max. 60 PSI
Cooling Water Flow	Min. 2.0, Nom. 3.0 GPM
Cooling Water Temperature at Inlet	Max. 86°F
Dimensions	31-1/2" w. x 24" h. x 19-1/2" d.
Weight	270 pounds

The manufacturer's instruction manual Model No. T-2.5-1-MC2-BW, Serial No. 7228J, Type No. T-252-53 is included with hardware returned to EPA under contract terms.

2.2 Drake RF Transmitter and ETO Linear Amplifier

The Drake RF transmitter is a typical tube-type "ham" radio operator transmitter which offers selectable single sideband, semi break-in CW, and controlled carrier AM transmission. The unit provides 200 watts PEP input on SSB and AM and 200 watts input on CW, which is ample power to drive the ETO linear amplifier. The following specifications apply to the Drake transmitter and to the ETO linear amplifier.

2.2.1 Drake Transmitter

Power Output	200 watts PEP in SSB and AM modes input power to final stage
Operating Frequency	3.5- 4.0 MHz 7.0- 7.5 MHz 14.0-14.5 MHz 21.0-21.5 MHz 28.5-29.0 MHz, all crystal controlled
Input Power	Supplied by Drake AC-4 power supply 120/240 VAC 50/60 cycles
Full Load Current	Approximately 5 amps
Cooling	None required
Dimensions	10-3/4" w. x 5-1/2" h. x 11-5/8" d.
Weight	14 lbs 1 oz.

2.2.2 ETO Linear Amplifier

Power Output	Input power to final stage is SSB mode: 3 KW PEP continuous CW mode: 1.25 KW continuous
Operating Frequency	3 to 30 MHz continuously variable over six ranges
Operating Power Requirements	115/230 VAC 50/60 Hertz single phase
Full Load Current	Approximately 15 amperes/230 VAC or 30 amperes/115 VAC
Cooling	A built-in fan is used for air cooling
Dimensions	17" w. x 9-1/2" h. x 18" d.
Weight	70 pounds

The manufacturer's instruction manual Model No. T-2.5-1-MC2-BW, Serial No. 7228J, Type No. T-252-53 is included with hardware returned to EPA under contract terms.

2.2 Drake RF Transmitter and ETO Linear Amplifier

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2.2.1 Drake Transmitter

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Operating Frequency	3.5- 4.0 MHz 7.0- 7.5 MHz 14.0-14.5 MHz 21.0-21.5 MHz 28.5-29.0 MHz, all crystal controlled
Input Power	Supplied by Drake AC-4 power supply 120/240 VAC 50/60 cycles
Full Load Current	Approximately 5 amps
Cooling	None required
Dimensions	10-3/4" w. x 5-1/2" h. x 11-5/8" d.
Weight	14 lbs 1 oz.

2.2.2 ETO Linear Amplifier

Power Output	Input power to final stage is SSB mode: 3 KW PEP continuous CW mode: 1.25 KW continuous
Operating Frequency	3 to 30 MHz continuously variable over six ranges
Operating Power Requirements	115/230 VAC 50/60 Hertz single phase
Full Load Current	Approximately 15 amperes/230 VAC or 30 amperes/115 VAC
Cooling	A built-in fan is used for air cooling
Dimensions	17" w. x 9-1/2" h. x 18" d.
Weight	70 pounds

The manufacturer's instruction manuals are included with hardware returned to EPA under contract terms.

2.3 AC Arc Discharge System

The AC arc discharge system consists of an asbestos cell containing the discharge electrodes powered by an external high voltage power supply. A circuit diagram for the AC power supply appears in Figure 2.

A detailed description of the power supply is as follows:

Variac	115 VAC input 10A max. 0-140 VAC output
Luminous Tube Transformer	
Primary input	115 VAC
Secondary output	15 KVAC
Maximum current at secondary	60 mA
Power output	0.9 KVA
Capacitor	0.001 μF at 50 KVDC or similar with at least 25 KVDC voltage rating

The Webb cell itself appears in Figure 3. Webb's original cell was constructed using "Sindayno," a British trade name for a high density asbestos. The MRC cell patterned after the Webb cell was made of "Electrobestos," a dense asbestos used for high voltage industrial welding and other purposes. Both types of asbestos are formulated to absorb a minimum of water, which would raise the conductivity and not permit the use of high voltages in forming arcs between the built-in electrodes.

2.4 Radio-frequency Discharge Tube

The RF discharge tube system is composed of three concentric quartz tubes (coolant, plasma, and sample injection) held in specially designed metal holders machined from 316 stainless steel and aluminum. The system was devised to facilitate replacement of broken or melted discharge tube and is shown pictorially in Figure 4. Design specifications of the holder are presented schematically in Figure 5. In Figure 4, the upper holder is typical of the type used with a 38 mm coolant tube, whereas the lower holder is used with a 20 mm coolant tube. Both holders use a 15 mm plasma tube and a 6 mm sample injection tube.

The entire discharge tube assembly is of a concentric tube design with three gas inlets. The center tube functions as the sample inlet. A discharge gas (air, helium, argon, nitrogen, etc.) is admitted tangentially into another tube surrounding the sample inlet. Another concentric tube surrounds both the sample and discharge gas tubes and serves to admit a cooling

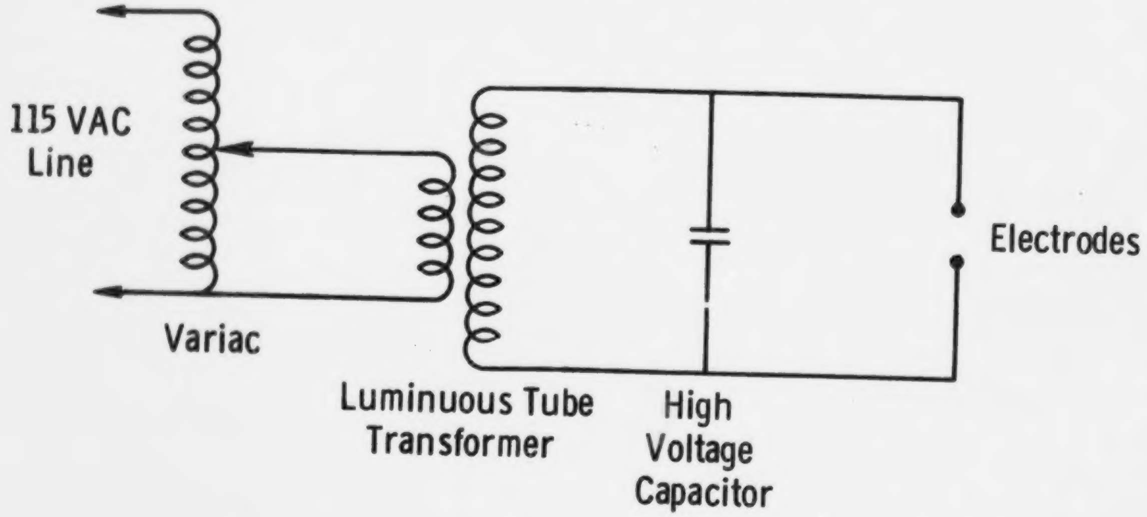
115 VAC
Line
Variac
Luminuous Tube
Transformer
High
Voltage
Capacitor
Electrodes

Figure 2. Electrical Schematic for AC Power Supply.

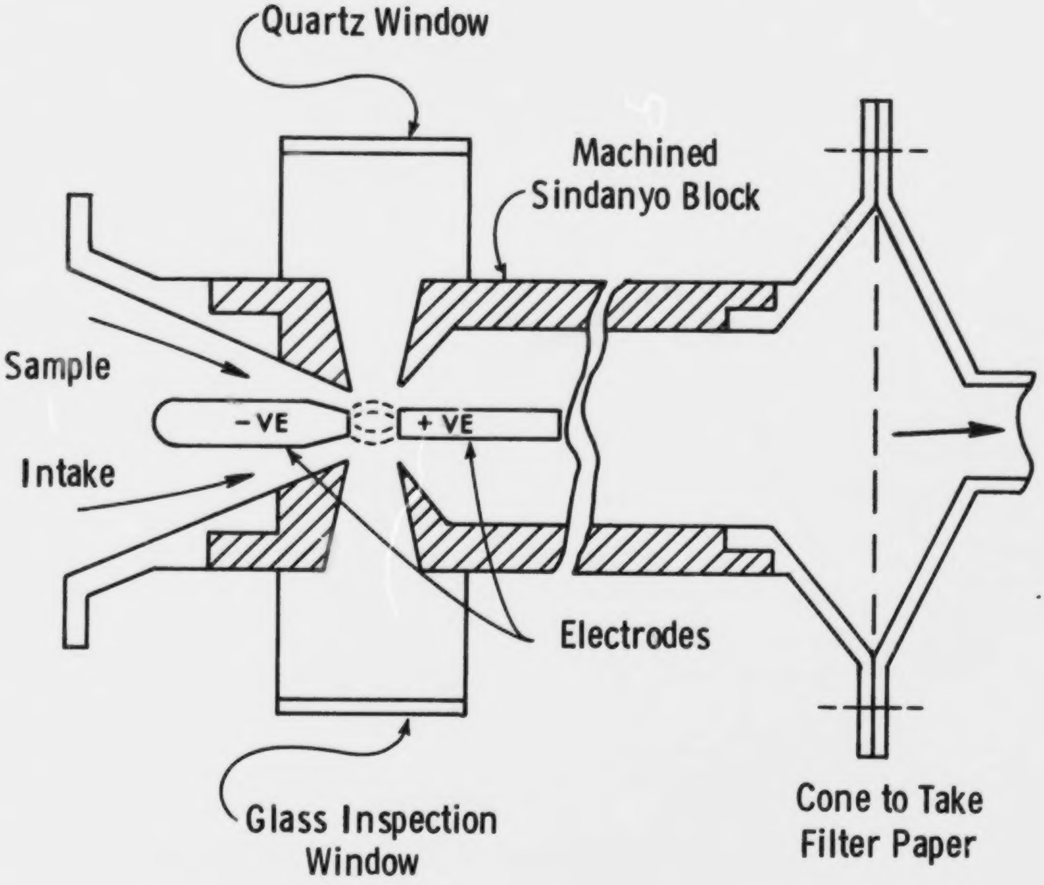
Quartz Window
Machined Sindanyo Block
Sample
Intake
-VE
+ VE
Electrodes
Glass Inspection Window
Cone to Take Filter Paper

Figure 3. Diagram of Webb-Type Arc Discharge Chamber

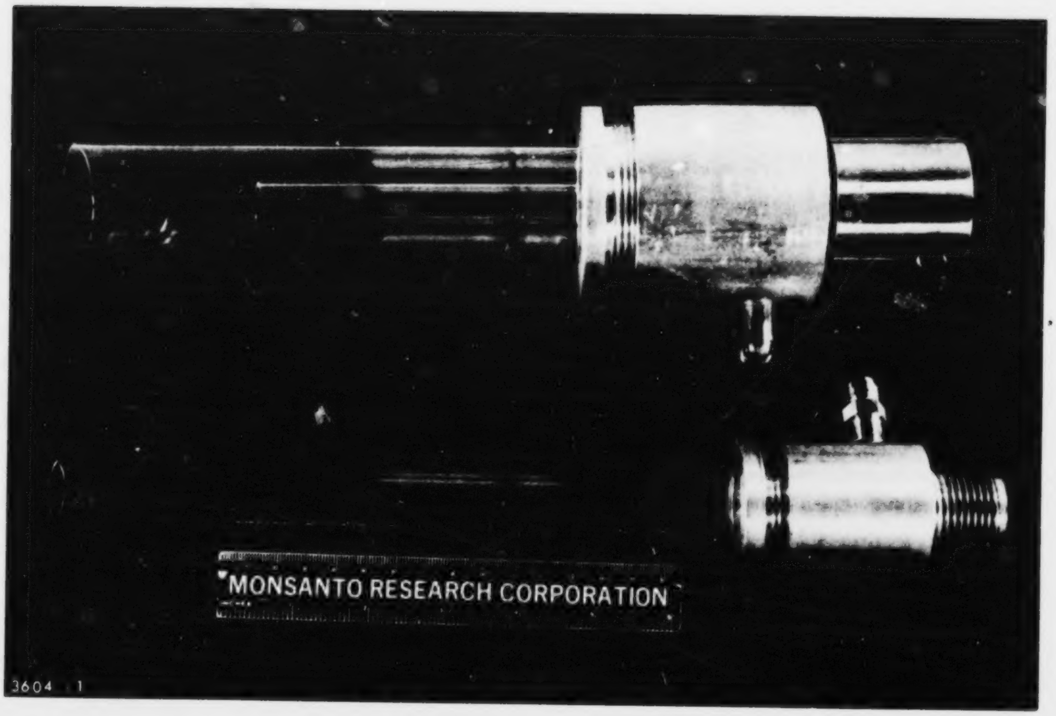
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Figure 4. Photograph of Radio-Frequency Discharge Tube

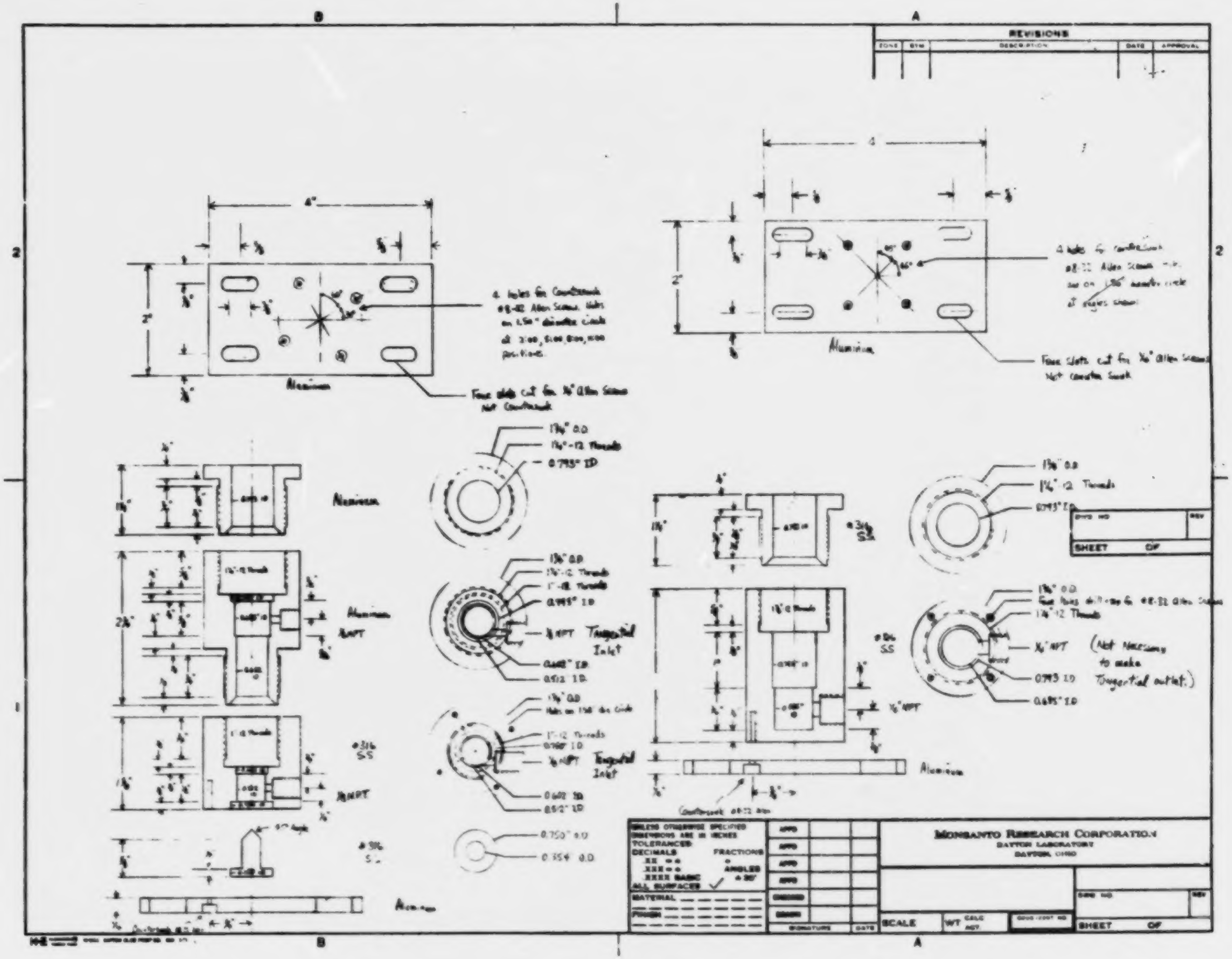

REVISIONS
ZONE
SYM
DESCRIPTION
DATE
APPROVAL
4"
2"
Aluminum
4 holes for Countersunk #8-32 Allen Screw, holes on 1.50" diameter circle at 2:00, 5:00, 8:00, 11:00 positions.
Four slots cut for 3/16" Allen Screw Not Countersunk
4 holes for countersunk #8-32 Allen Screws on 1.50" diameter circle at angles shown
Four slots cut for 3/16" Allen Screws Not countersunk
1 3/4" O.D.
1 1/4"-12 Threads
0.795" ID
1" -12 Threads
0.995" ID
1/8 NPT
Tangential Inlet
0.512 ID
Holes on 1.50 dia Circle
1"-12 Threads
0.602 ID
0.750" O.D.
0.354 O.D.
#316 SS
1/8 NPT
Four holes drill-tap for #8-32 Allen Screws
1/8" NPT
(Not Necessary to make Tangential outlet.)
0.795 I.D.
0.695" I.D.
Countersunk #8-32 Allen
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
ALL SURFACES
MATERIAL
FINISH
APPD
CHECKED
DRAWN
SIGNATURE
DATE
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
SCALE
WT CALC ACT
DWG NO
REV
SHEET
OF
A
B
1
2

Figure 5. Schematic Showing Design Specifications for Radio-frequench Discharge Tube Holders

gas to the system. This coolant gas is also admitted in a tangential manner. The sample and discharge gas tubes terminate within the main body of the discharge tube and the sample tube is also shortened so as to terminate within a few millimeters of the end of the discharge gas inlet tube. A two to four turn water-cooled induction coil surrounds the open end of the main discharge tube and is powered by the Lepel 2.5 KW high frequency generator operating at frequencies of 15 to 50 MHz. Stabilization of the discharge is attained by vortex gas flow. The tube radius required is highly influenced by the skin effect peculiar to RF induction heating. The energy is dissipated in a thin layer so that the radius should not be much greater than the thickness of the coupled layer. By operating at relatively high frequencies (∿30 MHz) and controlled gas flows, a toroidal shaped discharge may be formed. The cooler core provided by this geometry presents far less resistance to particulate injection into the inner regions of the discharge than the more uniform discharge geometry associated with lower frequency operation. Figure 6 illustrates this concept.

2.5 Monochromator and Photometric Detection System

2.5.1 Jarrell-Ash 0.25-Meter Monochromator

A 0.25-meter Jarrell-Ash Model 82-410 monochromator was used as the wavelength separation device for radiation emitted from the RF or AC arc excited materials. It is a low cost, small size, lightweight instrument suitable for portable or field use. The specifications are as follows:

Focal Length	0.25 meter Ebert design
Linear Dispersion	3.3 nm/mm with 1180 grooves/mm grating 1.65 nm/mm with 2360 grooves/mm grating
Aperture Ratio (speed)	*f*/3.5
Gratings (two supplied)	Ruled area - 64 mm x 64 mm Replicas - 1180 grooves/mm 2360 grooves/mm
Gratings Blazed at	300 nm and 600 nm
Resolution (half-band width at 313.1 nm)	Better than 0.3 nm in First Order with 2360 grooves/mm grating with 150μ slits
Slits	Two 150 micrometer slits, fixed
Wavelength Coverage	0 to 900 nm

The instrument manufacturer's operating manual is included with the hardware returned to EPA under the terms of contract.

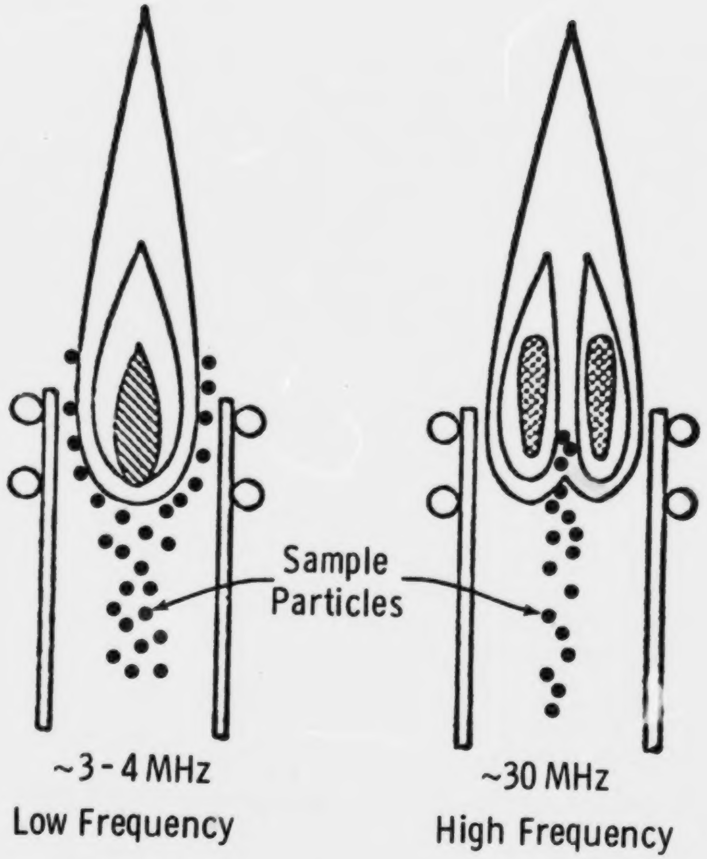

Sample
Particles
~3 - 4 MHz
Low Frequency
~30 MHz
High Frequency

Figure 6. Particulate Entrainment Into
Uniform vs. Toroidal Discharge

2.5.2 Photometric Detection System

Two RCA 1P28A photomultiplier (PM) tubes were housed in Pacific Photometrics Model 50F PM tube housing. One PM tube served as the sample tube and the other was the reference tube, as briefly described under the design concept in Section 1. A Bertran Model 602-11N power supply supplied the high voltage to the PM tube dynode chain.

An MRC designed and fabricated electrometer amplifier was used to monitor the PM tube currents. The amplifier was a differential, dual-channel design arranged to accept two PM tube inputs, one due to a sample and one to a reference, and to subtract the reference from the sample before display on a meter or optional strip chart recorder.

The sample channel incorporated a switch selectable range of input currents of 10^{-9} to 10^{-5} amps full scale in decade steps. Intermediate steps X1, X2, and X5 were also provided for each decade range. The reference channel had a fixed range of 0 to 10^{-6} amps full scale, and a 10-turn potentiometer at its output allowed subtraction of any current from 0 to 10^{-6} amps from the sample channel. A manual zero control (10-turn potentiometer) allowed adjustment of the electrometer circuitry to zero output with no current inputs.

In addition to real time spectral measurement capabilities, the electrometer had a built-in integrator allowing accumulation of PM tube currents over a manually controlled time period.

An auto zero circuit allowed zeroing the electrometer output in the spectral mode when observing only the background of an RF plasma or AC arc discharge with both the sample and reference PM tubes. With no material of interest (Be or Cd) undergoing emission, both PM tube channels should be equal and the electrometer output should be zero. When operating in the integral mode, the auto zero was set first in the spectral mode. Then an "integral zero" switch position allowed manual resetting of the integrator.

The time constant of the electrometer could be chosen and an appropriate low leakage capacitor used in the final amplifier stage of the electrometer. A front-panel meter indicator served to show the electrometer output, and a back panel recorder jack was provided to allow for permanent recording using a 1-mV input strip chart recorder.

2.5.2.1 Specifications MRC Signal Processor Unit

Signal Channel Input Current Sensitivity: For nominal 1.0 volt full scale signal output.

Range	Amps, Full Scale
10^{-5}	$0-10^{-5}$
10^{-6}	$0-10^{-6}$
10^{-7}	$0-10^{-7}$
10^{-8}	$0-10^{-8}$
10^{-9}	$0-10^{-9}$

Manual Zeroing Control: ±100% of full scale, independent of selected range.

Range Signal Channel: (When activated.) $0-2 \times 10^{-6}$ amps full scale; independent of range selected; adjustable from 0-100% of total available reference signal.

Automatic Baseline Correction: ±100% of selected range.

Signal Output Modes:

Spectral - Output signal voltage is linearly proportional to input signal current, with amplification factors of X1, X2, X5. Range indication is correct on X1 factor, increasing by X2 and X5 on other mode switch ranging.

Integral - Output signal voltage is time integral of input signal current. Increased sensitivity factors of X2 and X5 switch selectable.

Signal Output Readout: An adjustable voltage output signal for connection to any external potentiometric strip chart recorder with a span of 1-100 millivolts full scale may be used (output signal is positive signal with respect to ground, common).

2.6 Calibration System

2.6.1 Cadmium Vaporizer Probe

Calibration of the RF plasma system is based on the fact that cadmium is a relatively volatile metal. The vapor pressure of cadmium is about 1 mm of mercury at its melting point, 321°C. The metal vapor is normally generated at about 160°-200°C.

The cadmium metal is placed in a chamber constructed of black iron pipe and fittings. A Variac-controlled heating tape wrapped around the chamber with sufficient asbestos tape to insure even temperature control is monitored with a mercury thermometer. Inert gas, such as argon or nitrogen which contains no oxygen, is passed over the heated cadmium metal and carries the metal vapor out. The flow rate of the inert carrier gas must be low so that the metal vapor generating system is near equilibrium. An argon flow rate of 2.2 l/min with the cadmium metal at 160°-200°C gives 0.38-6.45 $\mu g/m^3$. This is a reasonable amount of cadmium vapor for calibration.

Attached to the exit of the vapor generating chamber is a heated injection probe. Its innermost tube, constructed of stainless steel, carries the cadmium metal vapor into the center of the plasma excitation region. Surrounding the innermost tube are two outer concentric copper tubes designed to circulate a cooling fluid through the entire probe assembly. Without the cooling fluid, the plasma would soon melt the probe tip.

Glycerol (glycerin, 1,2,3-propanetriol) is a satisfactory circulating cooling fluid. The injection probe must be maintained at a higher temperature than the temperature at which the cadmium metal vapor is generated, or else condensation in the stainless tube will soon plug it completely. The glycerol can be circulated at 220°-270°C with little difficulty. The glycerol circulation system is a heated constant temperature bath with a stirrer, a small centrifugal pump, and the necessary 1/4-in. copper tubing and fittings. Swagelok® fittings facilitate assembly and disassembly, and a portable hand-held heat gun and rubber pipet suction bulb may be necessary to initiate the flow of glycerol when starting a room-temperature system. The glycerol is very viscous at room temperature, but at about 150°C or more the viscosity approaches that of water and is no longer a problem to circulate through the small passages of the injection probe. A schematic of the entire assembly is shown in Figure 7 and the injection probe subsystem is shown pictorially and diagrammatically in Figures 8 and 9, respectively.

2.6.2 Beryllium and Cadmium AC Arc Discharge Calibration Assembly

To calibrate the AC arc discharge system, a beryllium or cadmium alloy wire is used as an electrode in a discharge cell placed above the analytical discharge cell. Metal vapor generated by the alloy electrode passes into the analytical discharge cell for excitation and system calibration. A gas filter (millipore type BDWB 04700) below the analytical cell is used to confirm the concentration of metal in the calibration vapor by atomic absorption spectroscopy. A schematic of the system is shown in Figure 10.

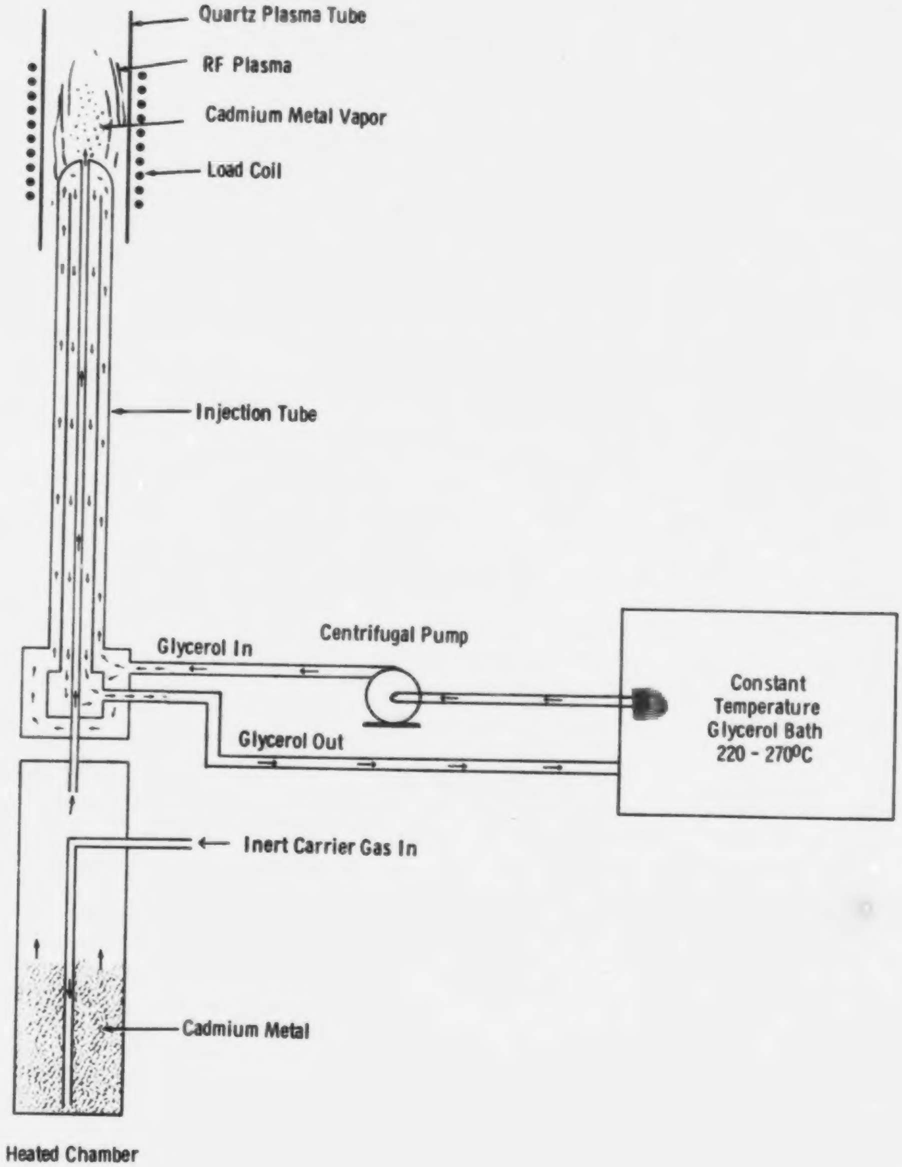

Quartz Plasma Tube
RF Plasma
Cadmium Metal Vapor
Load Coil
Injection Tube
Glycerol In
Centrifugal Pump
Constant Temperature Glycerol Bath 220 - 270°C
Glycerol Out
Inert Carrier Gas In
Cadmium Metal
Heated Chamber

Figure 7. Diagram Showing Complete Cadmium Vaporizer System for Injecting Cadmium Metal Vapor Into a Radio-frequency Plasma.

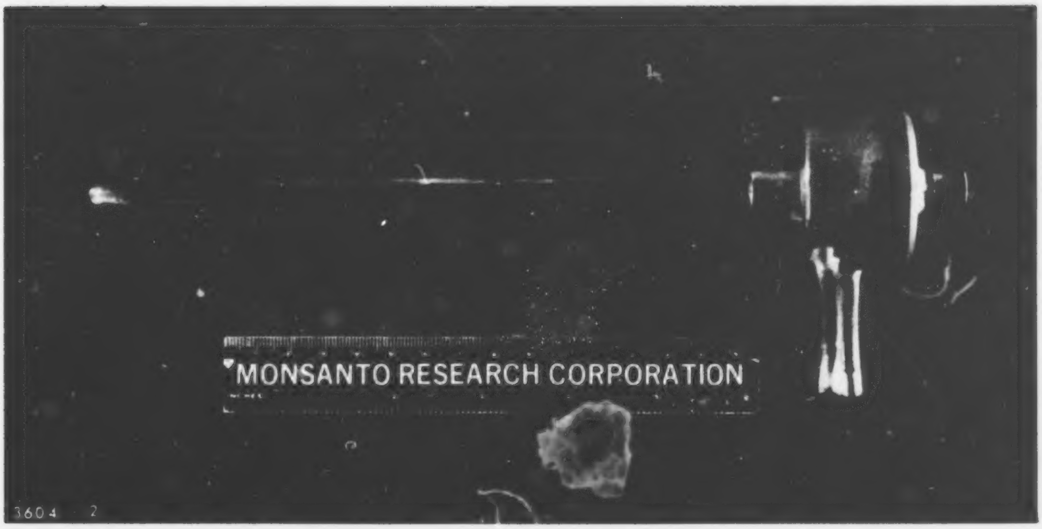

MONSANTO RESEARCH CORPORATION
3604 2

Figure 8. Photograph of Cadmium Vaporizer Probe for Injecting Cadmium Metal Vapor Into a Radio-frequency Plasma.

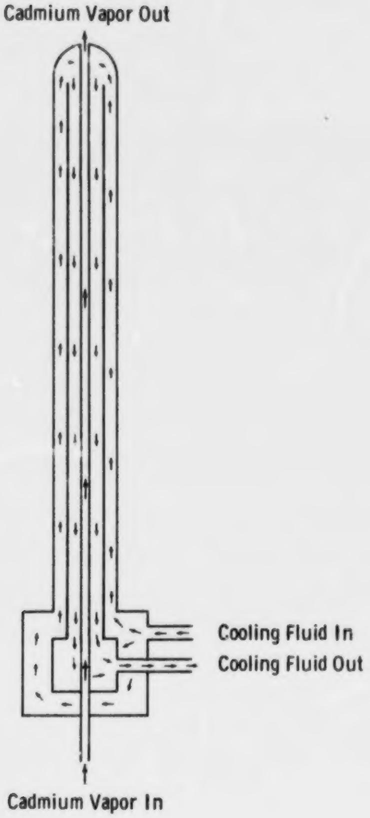

Cadmium Vapor Out
Cooling Fluid In
Cooling Fluid Out
Cadmium Vapor In

Figure 9. Diagram of Cadmium Vaporizer Probe for Injecting Cadmium Metal Vapor Into a Radio-frequency Plasma.

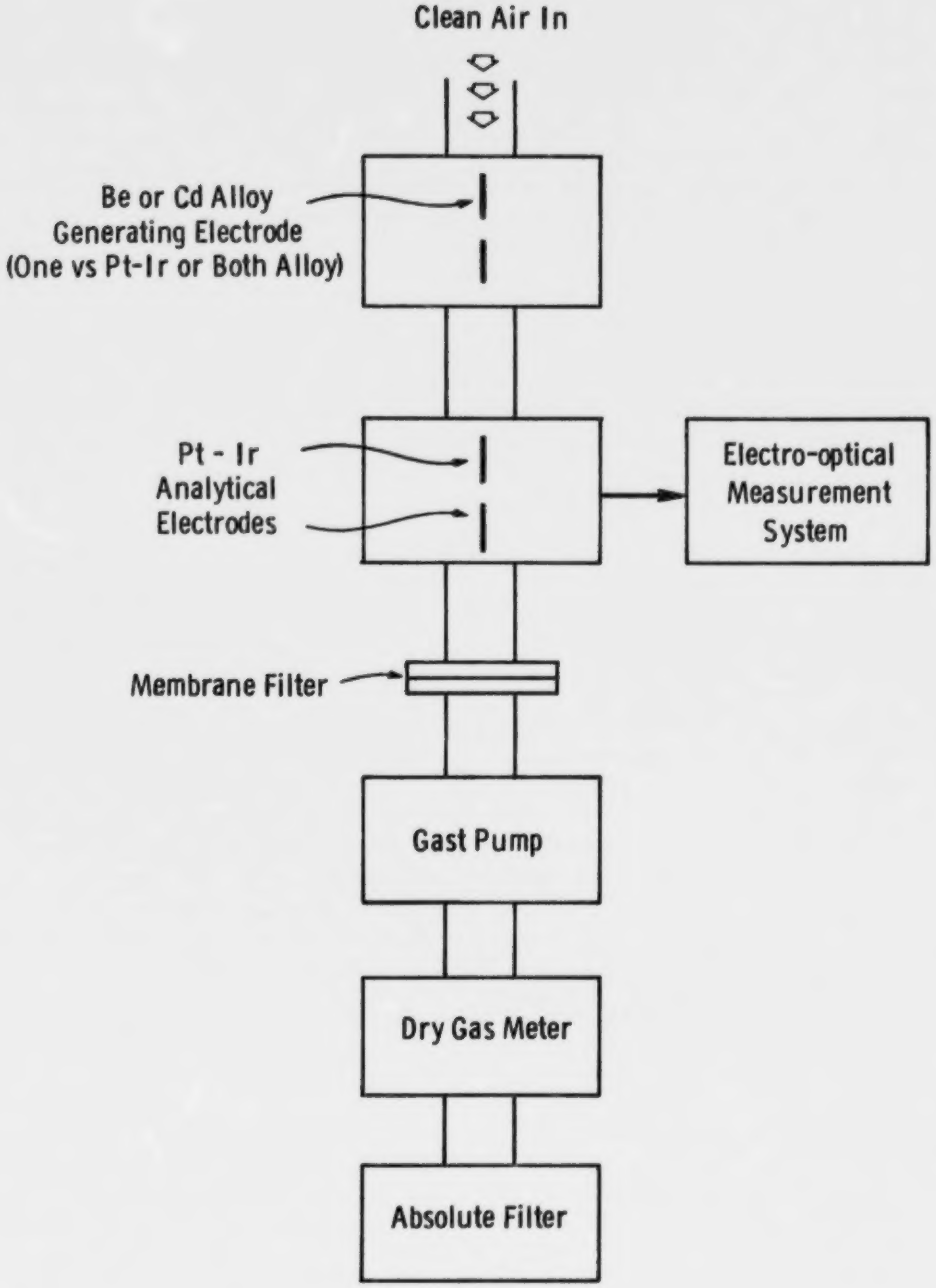

Clean Air In
Be or Cd Alloy Generating Electrode (One vs Pt-Ir or Both Alloy)
Pt - Ir Analytical Electrodes
Electro-optical Measurement System
Membrane Filter
Gast Pump
Dry Gas Meter
Absolute Filter

Figure 10. Diagram of Beryllium or Cadmium Calibration System Using Electrical Discharge to Generate Aerosols.

The beryllium electrode is 3/32-inch in diameter and is a 97% copper-3% beryllium alloy. The cadmium electrode is a silver brazing alloy rod #14 B&S wire gauge and containing 18% cadmium, 26% copper, 35% silver, and 21% zinc. The gap between generating electrodes can be 1 mm up to 10 mm with the wider gap requiring more voltage for initiation of the arc resulting in a hotter arc with more metal vapor generated. The power supply to operate the calibration electrode system is the same as the power supply to operate the analytical electrodes.

3. OPERATION PROCEDURES

Operation of individual subsystems are shown in respective manuals included with the deliverable hardware. Specific operational procedures are presented in the following subsections.

3.1 Method of RF Plasma Start-up

The RF plasma is impossible to initiate unless pure argon gas is used. The power control knob R3 (see Lepel manual, page 2-1) is set to its minimum position. However, it is not necessary to start the argon flow at this time. Push the start button, S3, and note the grid current (Meter M1) and plate current (Meter M2). When the power knob setting is slightly increased (do not exceed 10% power), both the grid and plate currents should increase simultaneously in a ratio of grid to plate of about 1:3 to 1:7. If grid and plate currents do not increase together (the plate current overload switch may automatically engage if current on the plate exceeds 830 ma; if it does engage, there is a 45-second delay before the start button S3 can be reengaged), adjust the grid and/or plate tank controls located at the right side of the generator. If the grid current decreases when the power is increased, turn the grid tank control to increase the grid current, or decrease the plate tank control. In order to operate at any specified RF frequency, an RF receiver is necessary to monitor the grid and plate tank control positions.

Once the grid and tank are properly adjusted, start a flow of argon gas of about 20 to 25 liters per minute in the plasma tube and increase the power control to about 25% (but do not exceed the grid or plate current maximum shown on the respective meters, 250 and 830 ma, respectively). The plasma will not self-initiate. One must use a Tesla coil held to the base of the quartz tube, or use a carbon rod (1/4-in. diameter and several inches long, similar to those used to make sample holders for arc spectroscopy) suspended by dry, nonconducting string down into the plasma tube in the region of the load coil. Be careful! Do not allow the Tesla coil to come near the load coil, and do not touch the carbon rod. RF energy is, like electric current, deadly if improperly respected or used. As an added precaution, do not touch any grounded objects when initiating the RF plasma by either of these methods.

Both methods of plasma initiation involve generation of free electrons in the plasma gas (argon). Once even a few free electrons are generated, and provided the generator and tuning and power controls are properly adjusted, an argon plasma is easy to initiate.

One must initiate the plasma with argon, but once initiated another gas such as air, nitrogen, etc., can be gradually added to the argon as the argon flow is decreased. Watch the grid and plate current meters and adjust the grid and tank controls accordingly as the new gas is added. Each plasma gas has a characteristic impedance and must be individually matched to the output impedance of the RF generator.

3.2 Procedure for Generating Cadmium Calibration Vapor

In order to generate cadmium vapor to calibrate the RF plasma, turn on the heating control for the vapor generating pot and turn on the heating unit in the glycerol constant temperature bath. Do not turn on the inert carrier gas at this time. Once the glycerol is warm enough that its viscosity lowers to approach that of water, turn on the circulating pump and use the pipet suction bulb (at the exhaust end where glycerol is returned to the constant temperature bath) to start glycerol flowing through the injection probe. The portable heat gun should be used whenever necessary to warm the glycerol in the probe, pump, or lines and reduce its viscosity. Once glycerol begins flowing, it will not cease unless allowed to cool until it becomes too viscous (maintain about 150°C or more). Once the glycerol is above the temperature of the cadmium vapor generating pot, the inert carrier gas may be turned on. Maintain the temperature of the glycerol above that of the cadmium metal vapor generating system or else metal will condense in the injection tip passage and block it.

3.3 Procedure for Generating Beryllium or Cadmium Calibrating Aerosols With Arc Discharge System

Attach the two asbestos cells, the membrane filter, the gas meter, and the Gast pump as shown in Figure 10 (Section 2.6.2). Attach the power supplies to both the aerosol generating and the analytical electrodes. Turn on both electrode systems and the Gast pump simultaneously by using a multi-outlet junction box with a single on-off switch. Measure the volume of gas using the gas meter and measure the amount of beryllium or cadmium aerosol generated by independently analyzing the material trapped on the membrane filter by atomic absorption spectroscopy. This calibration system should be operated for about ten minutes in order to collect sufficient material for analysis by AAS.

3.4 Operation of Monochromator and Photometric Detection System

Refer to the Jarrell-Ash manual for details of operation of the 0.25-meter Ebert monochromator supplied with the deliverable hardware. The physical placement of the emission source, signal PM tube, reference PM tube, PM tube high voltage power supply, monochromator, and electrometer is shown in Figure 1 (Section 1). A detailed operations manual for the MRC designed and fabricated signal processor unit will be found in the following sections.

3.4.1 Signal Processor Unit

The signal processor unit contains all of the electronic circuitry required to process and interface the detector with the readout device. It consists of a basic main frame section where all interconnections and control functions tie together the modular, plug-in, solid-state, printed circuit cards that accomplish the basic signal processing functions.

The processor is fabricated in a double shielded enclosure with adequate filtering of all input and output leads to permit operation in high power, ambient, radiofrequency fields developed by the RF excitation source. This heavy shielding is required to prevent RF saturation of highly sensitive electronic circuitry within the unit.

Basic circuitry to process the detector signal to a usable readout signal is contained on plug-in printed circuit modules. Descriptions of the five modules:

(a) Signal Electrometer Module (Model 9900.03)
(b) Reference Electrometer Module (Model 9900.04)
(c) Spectral Amplifier/Integrator and Automatic Baseline Correction Module (Model 8901.01)
(d) Amplifier Power Supply Module (Model 1100.01)
(e) Central Power Supply Module (Model 1200.01)

are presented in the following subsections. Schematics showing the electronic circuitry of the modules appear in Figures 11-16.

3.4.1.1 Signal Electrometer Module (Model 9900.03)

This module functionally transduces the signal detector output current to a voltage output which can then be differentially combined with three (3) other possible signals obtained elsewhere. These signals are the automatic baseline correction (auto zero), the background (reference) signal, and the manual zeroing signal (MZ). The circuitry consists of an electrometer, i.e., current to voltage transducer, A-200, in conjunction with range resistors R-101 through R-105 selected by range switch SW-101. Full scale current sensitivities of 10^{-5} to 10^{-9} amps

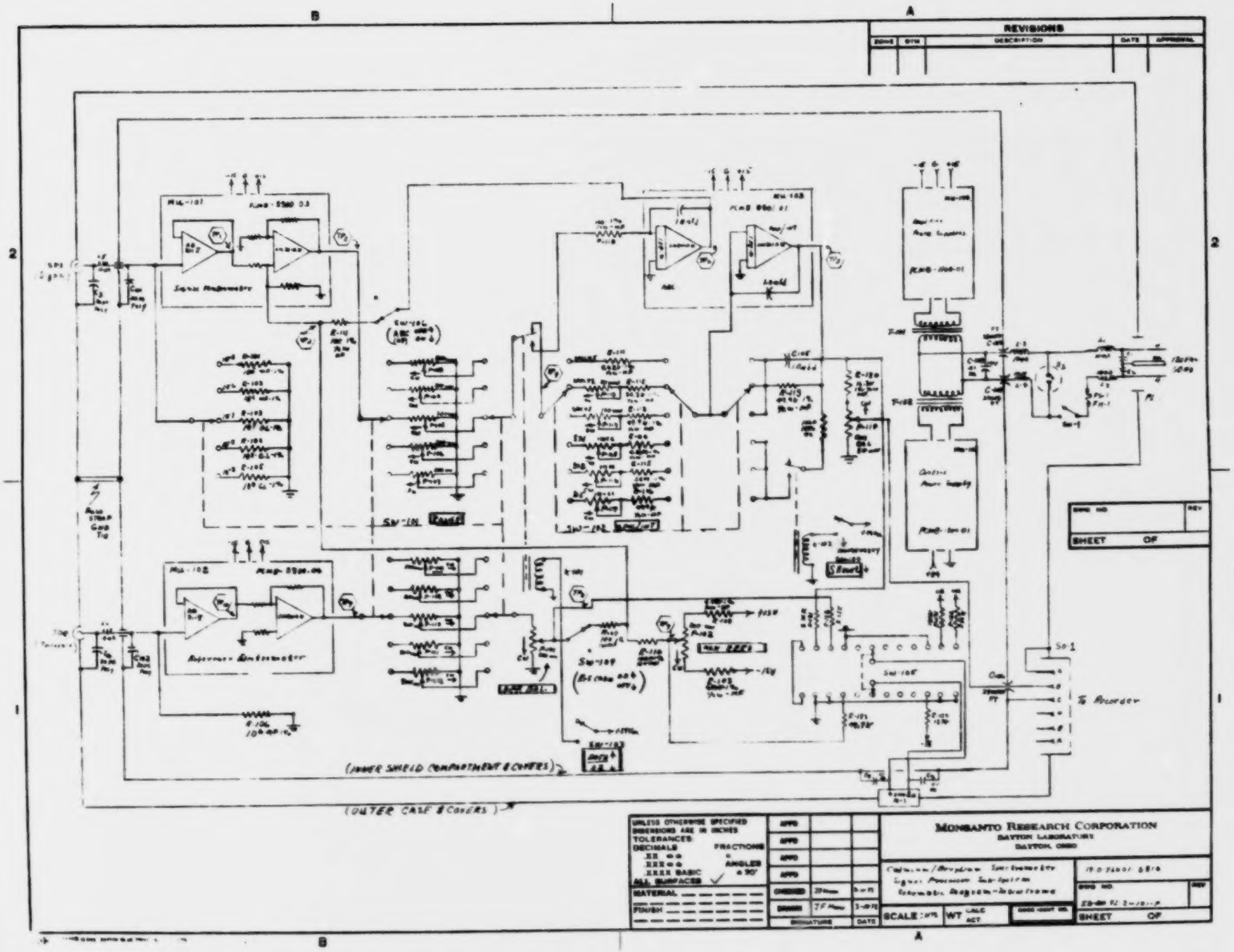

REVISIONS
ZONE
SYM
DESCRIPTION
DATE
APPROVAL
Signal Magnetometer
Reference Magnetometer
(INNER SHIELD COMPARTMENT & COVERS)
(OUTER CASE & COVERS)
To Recorder
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
ALL SURFACES
MATERIAL
FINISH
CHECKED
DRAWN
SIGNATURE
DATE
SCALE
WT
SHEET
OF
DWG NO
REV
A
B
1
2

Figure 11. Electronic Circuit Schematic - Signal Processor Unit - Main Frame

Reproduced from best available copy.

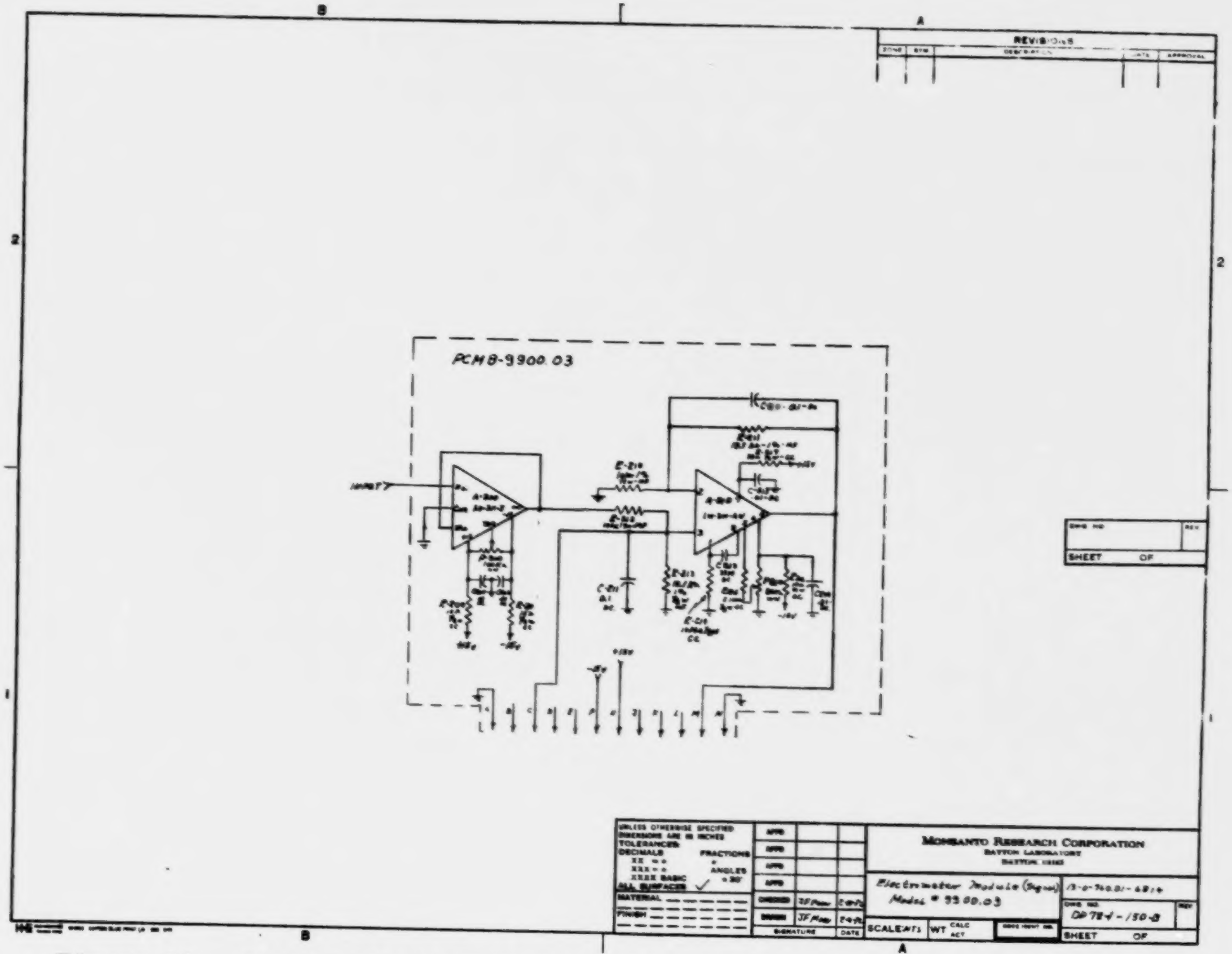

REVISIONS
PCMB-9900.03
INPUT
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
Electrometer Module (Signal)
Model # 9900.03
13-0-760.01-6814
DWG NO.
DP 784-150-B
SCALE
SHEET OF
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
MATERIAL
FINISH
CHECKED
DRAWN
SIGNATURE
DATE

Figure 12. Electronic Circuit Schematic - Signal Electrometer Module (Model 9900.03)

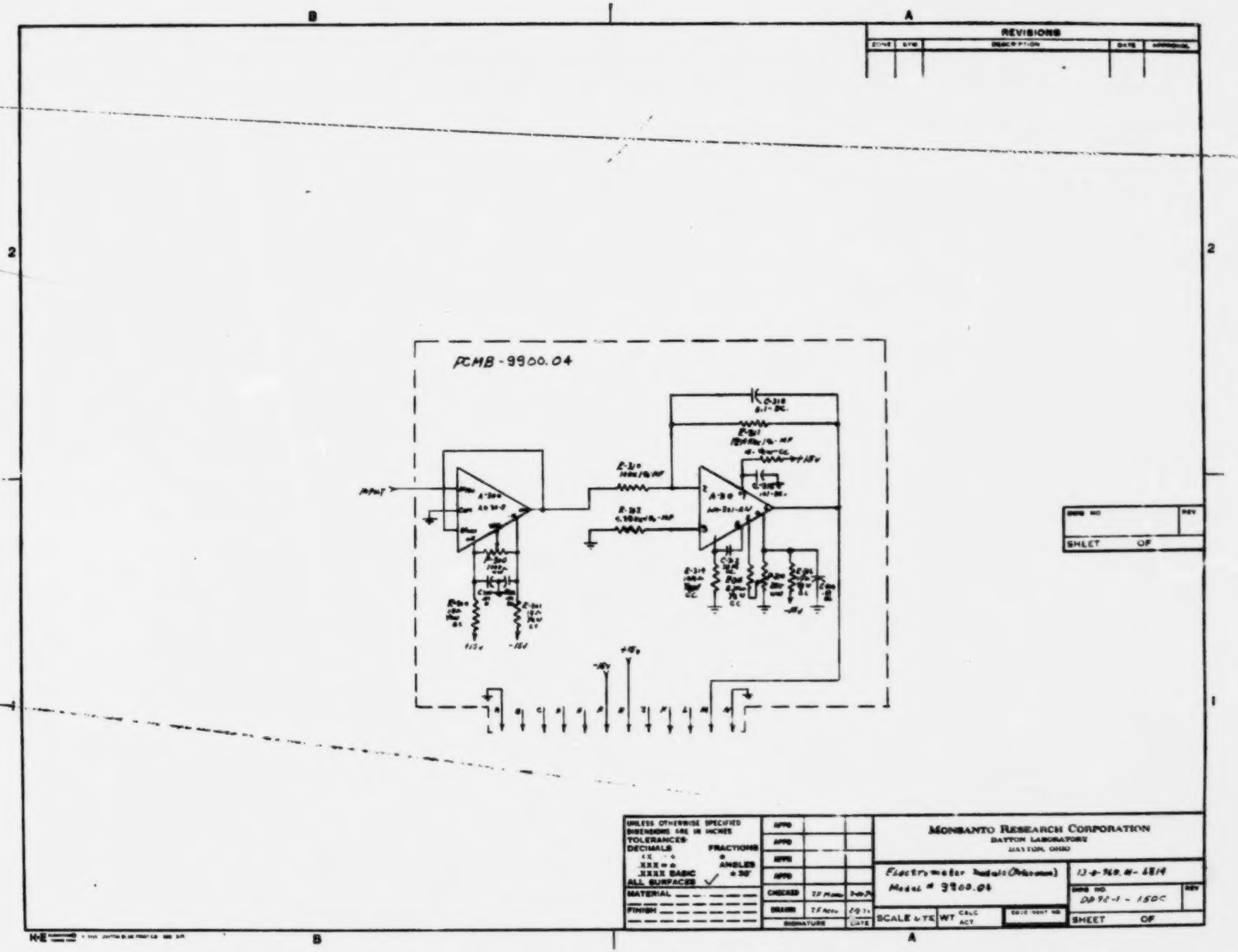

REVISIONS
PCMB-9900.04
INPUT
+15v
-15v
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
Electrometer Module
Model # 9900.04
DD 92-1 - 150C
SCALE
SHEET OF

Figure 13. Electronic Circuit Schematic - Reference Electrometer Module (Model 9900.01)

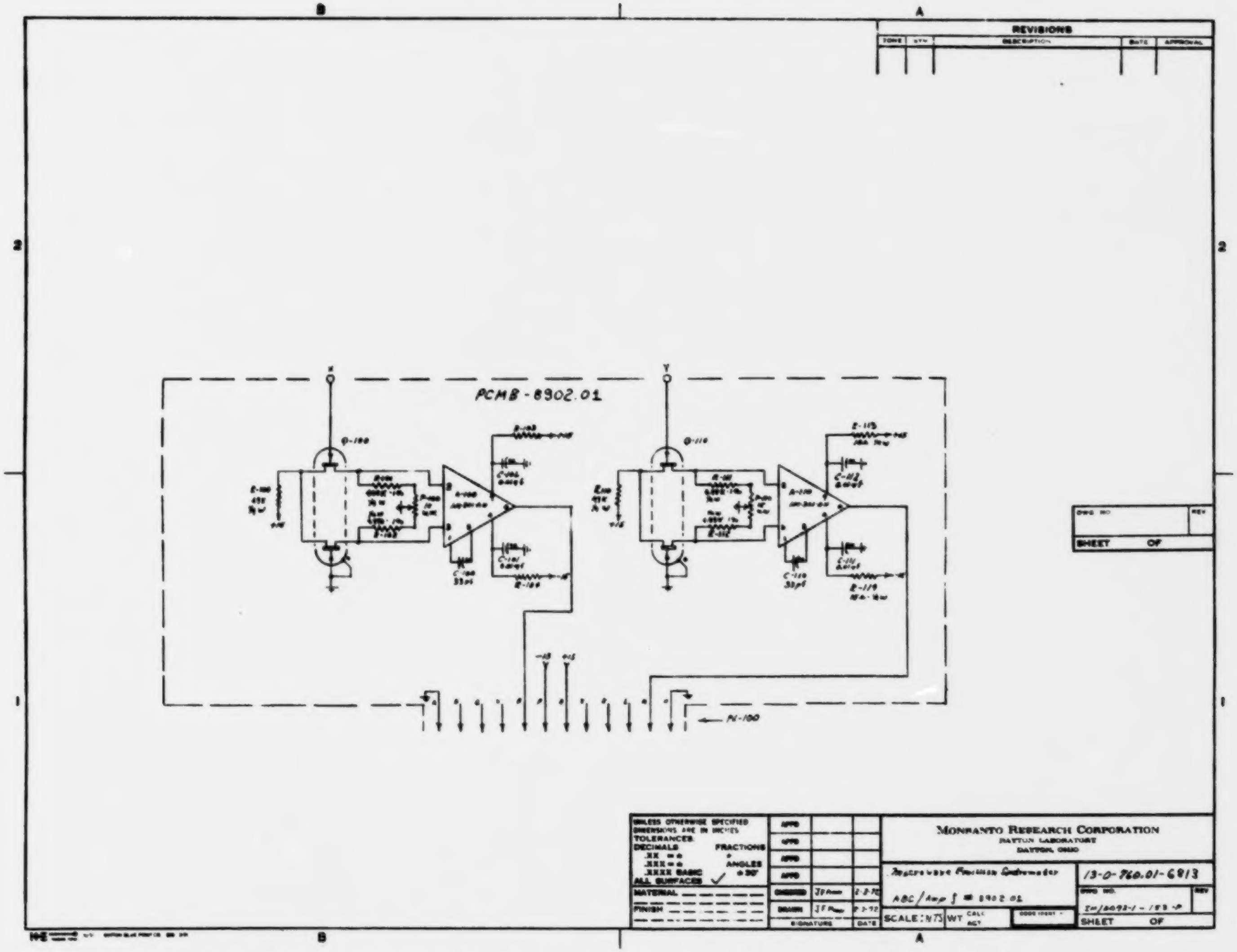
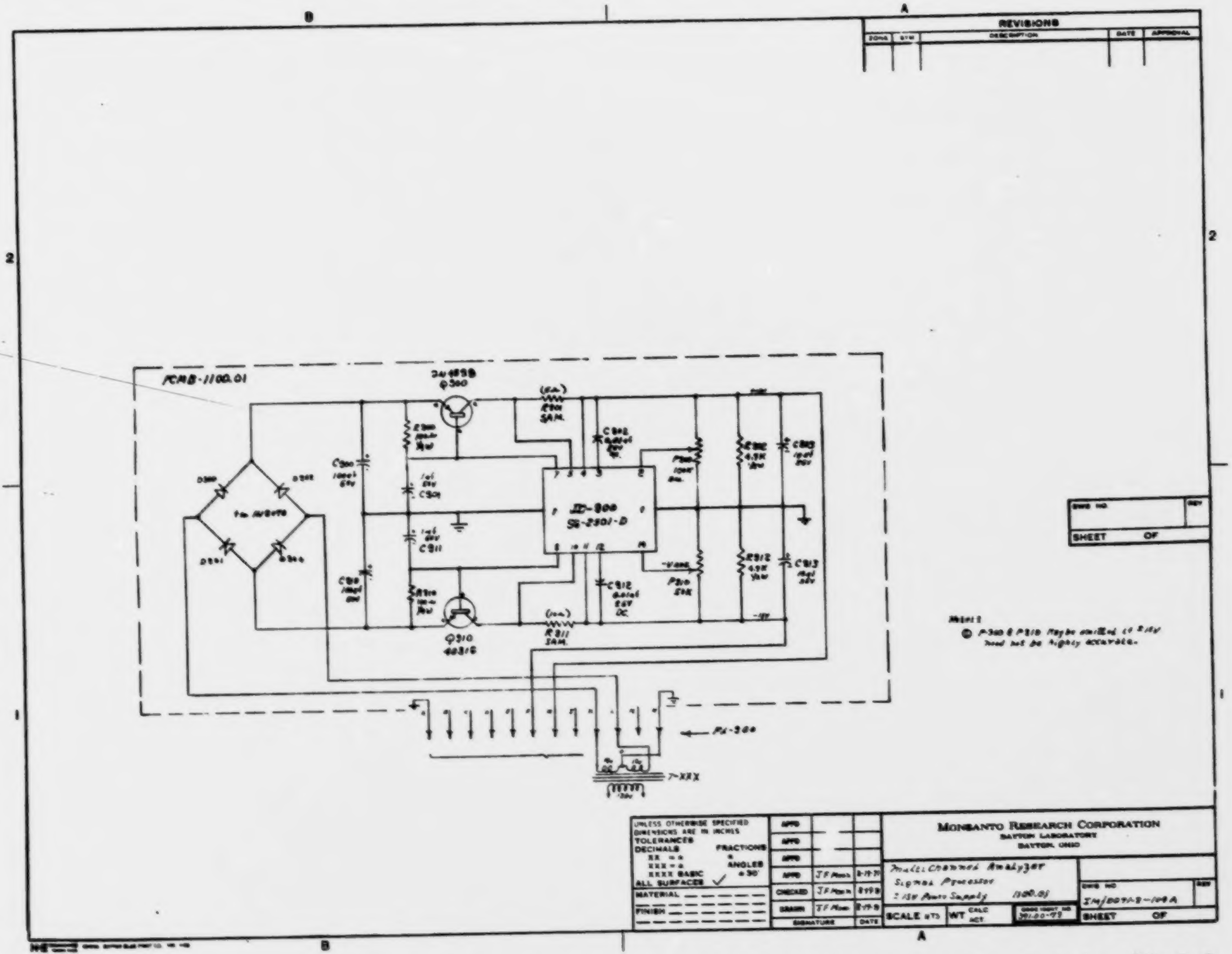
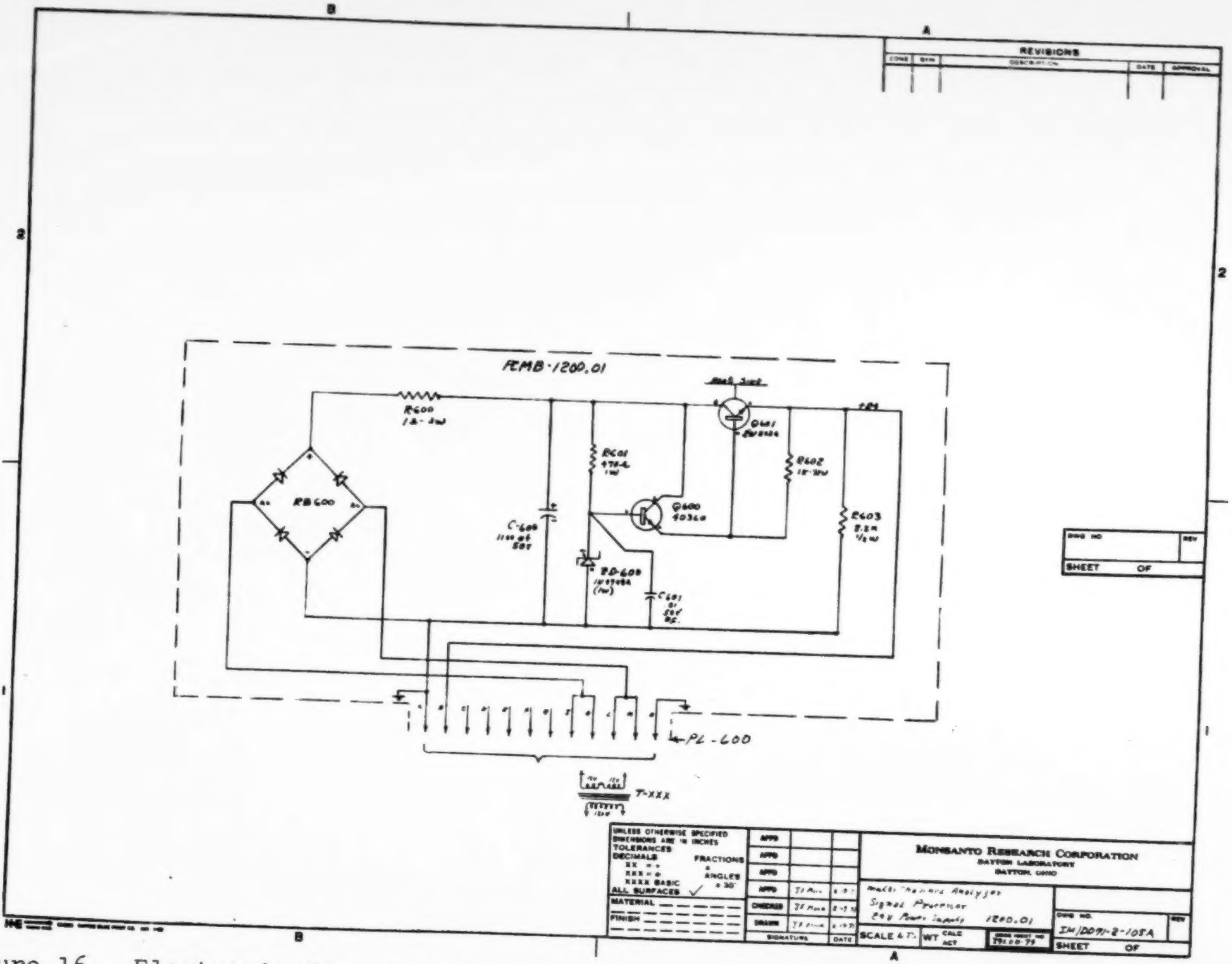

REVISIONS
ZONE
SYM
DESCRIPTION
DATE
APPROVAL
PCMB-8902.01
X
Y
Q-100
Q-110
C-100
33pf
C-101
C-102
C-110
33pf
C-111
C-112
R-104
R-113
R-119
-15
+15
PC-100
DWG NO.
REV
SHEET OF
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
ALL SURFACES
MATERIAL
FINISH
APPD
CHECKED
DRAWN
SIGNATURE
DATE
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
ABC / Amp ∫ # 8902.01
13-0-760.01-6813
SCALE: NTS
WT
CALC
ACT
SHEET OF
A
B
1
2

Figure 14. Electronic Circuit Schematic - Spectral Amplifier/Integrator and Automatic Baseline Correction Module (Model 8901.01)



REVISIONS
ZONE
SYM
DESCRIPTION
DATE
APPROVAL
FCMB-1100.01
2N4898
Q300
Q310
40316
R300
R301
R310
R311
SAM.
C300
C301
C302
C310
C311
C312
C313
D300
D302
D301
D304
IV-800
SG-2301-D
P300
P310
50K
R302
R312
4.9K
-15V
PL-300
T-XXX
NOTES
① P300 & P310 Maybe omitted if Bias need not be highly accurate.
DWG NO
SHEET OF
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
ALL SURFACES
MATERIAL
FINISH
APPD
CHECKED
DRAWN
SIGNATURE
DATE
J F Mann
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
Multi Channel Analyzer
Signal Processor
± 15V Power Supply 1100.01
SCALE
WT CALC ACT
SHEET OF

Figure 15. Electronic Circuit Schematic - Amplifier Power Supply Module (Model 1100.01)



REVISIONS
ZONE
SYM
DESCRIPTION
DATE
APPROVAL
PCMB-1200.01
R600
1Ω-3W
RB600
C-600
1100 μf
50V
RC01
47Ω
1W
ZD-600
1N4748A
(1W)
C601
.01
50V
DC.
Q600
40360
Q601
2N3054
R602
1K-½W
R603
8.2K
½W
+24
PL-600
T-XXX
DWG NO
SHEET OF
REV
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES
DECIMALS
FRACTIONS
ANGLES
XXXX BASIC
ALL SURFACES
MATERIAL
FINISH
APPD
CHECKED
DRAWN
SIGNATURE
DATE
MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
DAYTON, OHIO
Multi-channel Analyzer
Signal Processor
24V Power Supply 1200.01
SCALE
WT CALC ACT
DWG NO.
IM/DD91-2-105A
SHEET OF
REV
A
B
1
2

Figure 16. Electronic Circuit Schematic - Central Power Supply Module (Model 1200.01)

per volt output are selected by the range switch. Amplifier A-210 provides a voltage gain >1 for the electrometer output voltage signal. Passive output attenuation P-103 through P-107 provide for exact calibration of each range selected. The other previously mentioned signals are applied differentially to A-210. The reference signal obtained from a similar electrometer circuit can be adjusted to cancel out continuum background where it exists, leaving only the desired signal. The manual zero can be adjusted to cancel out static dark current in the photomultiplier detector. The automatic baseline correction can be used to account for shifting or drifting of any of the above signals and can be activated at any desired time by the operator. The auto baseline correction (ABC) can be disabled, if so desired, as can the reference signal by operation of switches located on the internal subchassis. Overall, the circuit is noninverting, polaritywise.

3.4.1.2 Reference Electrometer Module (Module 9900.04)

This module functionally transduces the reference detector output current to a voltage output which is one of the possible differential signals applied to the signal channel electrometer module. It is a single range unit with individually adjustable output voltage for each range. This offers high versatility in the application of this signal.

Amplifier A-300 is the basic electrometer, cascaded with gain block A-310. The circuit overall is an inverting configuration so that differential action can be obtained in A-210 on the signal electrometer module.

3.4.1.3 Spectral Amplifier/Integrator and Automatic Baseline Correction Module (Model 8901.01)

This module functionally accepts the resultant output signal from the signal electrometer module and processes it to the best usable form depending on the type of sampling technique used. Continuous sampling suggests use of the spectral mode. Batch, or spot, sampling technique can use the spectral operational mode, but a possible better mode is the integral mode of operation. The output signal voltage is the time integral of the sample concentration equivalent detector current.

Switching is incorporated to select the spectral or integral mode. This switching further provides gain enhancement of amplifier/integrator Q-110/A-110, by factors of X2 or X5 over the basic current sensitivity obtained with X1 operation, either in the spectral or integration modes. All mode switching functions are obtained by SW-102. Relay K-102 provides for resetting the integrator circuit to zero conditions. The output signal can be connected to an accessory strip chart potentiometric recorder with any full scale span of 1 to 100 millivolts. Recorder span is adjusted to the unit by attenuator P-118. The output signal is positive for current into the signal electrometer input.

It is highly desirable to have a zero output voltage signal with no sample at the detector. An additional circuit contained on this module is the automatic baseline corrector circuit, providing a zero output voltage signal with no sample present. This is also a requirement of the input signal for the integrator circuit, i.e., to prevent false integrals, input voltage other than zero must be cancelled out. The circuit to accomplish this feature consists of Q-100/A-100 forming an additional integrator circuit. This circuit is activated whenever panel switch SW-103 is placed in the AZ (auto zero) position, energizing relay K-101. When K-101 is energized the ABC integrator is connected in a loop-feedback circuit and will integrate in such a way as to drive its own input back to zero volts. This redrive signal is one of the differential signals applied to the signal electrometer module. The circuit will follow variations always keeping its input at zero volts. When SW-103 is activated to the data position (sample also introduced) K-101 de-energizes and the ABC integrator holds the value of voltage required to zero the unit in memory. The sample signal now is connected to the spectral/integrator amplifier input. Only that signal voltage value over and above background signal and dark currents is then processed, either in spectral or integral form.

3.4.1.4 Amplifier Power Supply Module (Model 1100.01)

This module provides dual, highly regulated, voltages to the electrometers and integrated circuit amplifiers on the other modules. Good regulation is required to prevent circuit drift and instability.

3.4.1.5 Control Power Supply Module (Model 1200.01)

This module provides regulated voltage for operation of the relays in the unit.

3.4.1.6 Performance Monitor

A panel meter is provided to give readout of operating voltages for the unit as well as signal output voltages.

4. MAINTENANCE/ADJUSTMENTS/CALIBRATION OF MRC SIGNAL PROCESSOR UNIT

The following section contains instructions for unit maintenance. Maintenance and adjustments for calibration should only be performed by personnel thoroughly familiar with the technique involved. This requires an experienced electronic technician familiar with analog test procedures. Adjustments on the analytical subsystem requires personnel experienced in photometric techniques.

For performance to meet specifications, a logical stepwise procedure must be employed to test or troubleshoot problem performance. The following sections are outlined in this form.

4.1 General Maintenance Suggestions

The electronic circuitry provided has some inherent testing capability which can be used for quick checks on portions of the instrument operations. These are of use both for the operator and for the maintenance technician. These tests can be performed at any time. It is good practice to record analog meter test readings. If the instrument parameters after initial specified operation are confirmed, a basis is then available for future comparisons. As with all electronic instruments, some deviations will occur with aging and environmental conditions such as shifting ambient temperature. Small deviations can be cancelled by adjustments with front panel controls. Gross deviations generally indicate a circuit failure or improper operating technique.

Troubleshooting for circuit failures should only be performed by knowledgable, experienced personnel. Recalibration should not be attempted except after thorough study of the instrument.

Repairs on the printed circuit boards require the use of a "solder sucker" type iron to remove defective components. The wattage rating should not exceed approximately 50 watts. Replacement parts should be resoldered with a small tipped iron not to exceed 50 watts dissipation. The holes in the P.C. board should be completely free of old solder before the new component is installed. Do not force leads through the holes. Do not overheat the component or circuit foils when resoldering. Do not use excessive solder. Use only 60/40 tin/lead rosin core solder for repairs. Use of heat sink clips is recommended in all cases possible. Residue flux can be removed with a brush and toluene. Avoid excessive application of toluene as component markings may be destroyed.

One final general word of caution: Avoid touching the range switch, the range resistors, and the electrometer circuit boards, as well as the components and the P.C. board in the area of the summing points of the signal integrator/amplifier and the automatic baseline correction circuit. Fingerprints or generally dirty conditions can cause these circuits to perform outside of specifications.

Detailed troubleshooting and recalibration require the use of external test equipment of known accuracy and precision. The following equipment is recommended:

1. Digital multimeter capable of resolution to 1 mV and having high input impedance. (Almost any "name brand" meter on the market meets these requirements). An analog meter may be used, but they generally lack the degree of readout resolution desired.

2. A variable "voltbox" capable of output range of 0 to ±1000 μV minimum range and having a resolution of less than 100 microvolts. Another desirable feature is the inclusion of a range resistor(s) for electrometer testing.

3. Laboratory grade potentiometer with a resolution of less than 10 microvolts. While not required, it is useful for electrometer tests especially if the "voltbox" is not available.

4.2 Generalized Troubleshooting Procedure

Efficient troubleshooting of operational problems should follow the generalized steps listed below. No description of troubleshooting procedures can give complete coverage of all possible problems and tests, but they can serve as a guide to assist maintenance and operating personnel. Familiarity with overall circuit functions is paramount for effective maintenance. Most malfunctions in this type of analog circuitry manifest themselves as saturation at circuit voltage limits, either positive or negative, or as drifts in output voltage levels with time.

A. Localize the Problem Area - Performance Test Meter Monitoring

1. Disconnect the signal and reference input cables on the rear panel of the processor unit.

2. Rotate the test meter switch through its positions and note the presence, absence, or deviations from normal readings of the power supplies. Compare the readings with those obtained when unit was operational. Deviation from these normal readings indicate the possible problem area. Troubleshoot any area where a malfunction is indicated. If no malfunction is indicated by the meter readings, proceed to step B.

B. Systematic Test Procedure

This test procedure can help localize troubles in the signal processor unit.

1. Set the panel controls as follows:

a.	Data/Auto Zero	DATA
b.	Spectral/Integral	Spectral X1
c.	Panel Meter	B
d.	Manual Zero	500
e.	Range Switch	10^{-6}

2. Set the internal controls as follows:

a.	Reference Channel	OFF
b.	ABC (AZ)	OFF

3. Connect test digital voltmeter to TP-1.
   a. Reading should be 0.000 ± 0.050 volts DC
      (1) If reading exceeds ±0.050 volts, adjust P-200 on signal electrometer for zero reading - 0.000 ± 0.010 volts DC
      (2) If reading is not adjustable and is approximately ±14 volts DC electrometer amplifier A-200 is faulty.
      (3) If unit is in specification or can be adjusted to specification, proceed to step 4.
4. Connect DVM to arm of manual zero control (TP-9) and adjust control for 0.000 ± 0.010 volts DC
5. Connect DVM to TP-2. Reading should be 0.000 ± 0.050 volts DC. If reading exceeds ±0.050 volts, adjust P-210 on signal electrometer for 0.000 ± 0.010 volts DC.
6. Set range switch to 10^{-9}. Reading at TP-2 should be 0.000 ± 0.050 volts DC. If reading exceeds ±0.050 volts DC, carefully readjust P-200 for 0.000 ± 0.010 volts DC.
7. Set range switch to 10^{-6}. Connect PVM to TP-5. Reading at TP-5 should be 0.000 ± 0.050 volts DC. If reading exceeds ±0.050 volts DC, carefully adjust P-110 on the amplifier integrator module to 0.000 ± 0.005 volts DC.
8. If all preceding tests are valid, unit should operate correctly.

9. Rotate manual zero control clockwise. Panel meter should go upscale. If meter "follows" control, unit is operational from electrometer differential amplifier through the output amplifier. Reset control for zero output reading on panel meter and recorder.

C. Input Signal Test

1. Leave DVM connected to TP-5.

2. Connect negative output of voltbox or laboratory potentiometer to center conductor of SO-3 through 1.00 megohm 1% resistor. Set output to -1.000 volts DC Connect positive output to processor chassis. Panel meter should read 50 (1/2 full scale). Recorder should read 1/2 full scale. DVM should read +0.500 volts DC.

3. Reduce voltbox or potentiometer input voltage to 0.000. Panel meter, recorder and DVM should be at 0.00.

D. Test of Reference Electrometer

1. Connect DVM to TP-10, panel meter switch to "C". Reading should be 0.000 ± 0.050 volts DC.

   (a) If reading exceeds ±0.050 volts DC, adjust P-300 on reference module for 0.000 ± 0.010 volts DC.

   (b) If reading is not adjustable and is approximately ±14 volts DC, electrometer amplifier A-300 is at fault.

2. Connect DVM to TP-7. Reading should be 0.000 ± 0.050 volts DC. If reading exceeds ±0.050 volts DC, adjust P-310 on reference module for 0.000 ± 0.010 volts DC.

3. Leave PVM connected to TP-7.

4. Connect negative output of voltbox or laboratory potentiometer at -1.000 volts DC through 1.00 megohm, 1%, resistor to center post of SO-2. Connect positive output to processor chassis.

   (a) DVM should read 1.000 ± 0.020 volts DC.

   (b) Panel meter reading will depend on calibration setting of P-109 and setting of reference balance control P-101. Reading should be maximum with reference balance control completely counter clockwise.

5. Set reference balance at 1000 count. Turn SW-107 so that reference channel is activated. Reverse recorder lead wires. With -1.00 voltbox input through 1.00 megohm resistor still connected, advance reference balance control toward 000 count (CCW). Recorder should go upscale. Meter "C" will go upscale. If both respond, reference channel is operable. Disconnect input signal. Return recorder wires to original configuration.

This completes the test procedure. If all responses were as described, unit is in good operating shape except for possible calibration errors.

4.3 Unit Calibration

Calibration requires an accurate source of voltage and the use of precision resistors and should not be attempted without complete understanding of the unit circuitry. The test input signal used in the troubleshooting procedure 4.1.C gives a partial indication of calibration precision on one range only. If total recalibration is required, it is suggested that the user contact Monsanto Research Corporation for authorization to return unit for calibration.